WATER AND SOLUTE TRANSPORT IN LAKELAND FINE SAND

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1974

DEDICATED

TO THE MEMORY OF MY FATHER, WHOSE

SILENT PRESENCE WAS GUIDED MY

EFFORT

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Dr. Robert S. Mansell, Chairman of the Supervisory Committee, for his valued counsel, guidance, and assistance throughout the entire course of this study, and for his valuable suggestions and excellent assistance and above all for continued moral support during the entire duration of the program.

The author is indebted to Dr. Luther C. Hammond, Dr. Lucian W. Zelazny, Dr. Allan R. Overman, Dr. Willis B. Wheeler, and Dr. Wallace S. Brey, Jr., for their interest, constructive review of this manuscript and participation on the supervisory committee.

The author would like to recognize a long-time friend and brother, Dr. M.M. Selim. Sincere appreciation and gratitude are expressed for his assistance and support and special thanks are due for his help in doing the calculated results of this study.

Gratitude is expressed to Dr. Charles F. Eno, Chairmen, Soil Science Department, for arranging the facilities for graduate study.

To Dr. James M. Davidson appreciations are extended for his invaluable help and support.

Special thanks are due for Mr. Richard M. McCurdy for his help in the Soil Physics Laboratory and to Mr. Ronald E. Jessup for his words of encouragement.

The author is grateful to the Florida Water Resources Center for financial support through the U.S. Department of the Interior, Office of Water Resources Research Project Number A-026-FLA and to the Soil Science Department, University of Florida for partial support.

Special recognition is given to my fellow graduate students Renaldo de la Cruz, John J. Nicholaides, Pimpan Kanchanasut, and José L. Mesa

for the scientific and human enrichment of their friendship.

The author wishes to commend Mrs. Kathryn B. Anderson and Mrs. Nadie Scheffer for excellence and dedication in typing and proofing the final copy of this dissertation.

The author is indebted to Dr. Luther C. Hammond for arranging the computer time and to Dr. Willis B. Wheeler for his assistance in Thin Layer Chromatography work.

The author wishes to thank my friends Mike Wedel, Riley Burns, and the Burns family for just being themselves.

Last, but by no means least, to my mother, brothers Adel, Asem, Amer, Aref, Akef, and my sister, Awatef for their encouragement and assistance goes a most personal acknowledgement.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	iii
LIST OF TABLES	vii
LIST OF FIGURES	viii
ABSTRACT	xi
INTRODUCTION	1
LITERATURE REVIEW	3
THEORY	13
Water and Solute Flow Equations	13
Finite Difference Approximation for Water and Solute Flow Equations	16
Numerical Solutions of Water and Solute Equations	16
Initial and Boundary Conditions	18
NATERIAL AND METHODS	21
Soil Sampling	21
Soil Analyses	21
Physical Setup of Soil Column Flow System	22
Preparation of the Flow Column	24
Water Content and Bulk Density Measurements	25
Soil Water Pressure Measurement	27
Preparation and Analysis of Solute	28
Solute Adsorption Isotherm and Kinetics	30
Solute Dispersion Coefficient Measurement	31
Degradation of 2,4-D in the Columns	31
RESULTS AND DISCUSSION	33
Soil Analyses	33
Degradation of 2,4-D in the Columns	40
Rate of 2,4-D Adsorption	43
2,4-D Adsorption and Desorption Isotherms	43
Soil Water Measurement	46
Dispersion Coefficient Analyses	48
Column Packing	53
Movement of Water, Chloride, and 2,4-D	55
The Effect of Surface Water Flux	55
The Effect of Initial Soil-Water Content	85
SUMMARY AND CONCLUSIONS	83
APPENDIX	90

TABLE OF CONTENTS (Continued)

Page

LITERATURE CITED 96

BIOGRAPHICAL SKETCH 102

LIST OF TABLES

Table		Page
1.	Selected physical properties of Lakeland fine sand	34
2.	Particle size distribution of Lakeland fine sand	35
3.	Pore size distribution of Lakeland fine sand	36
4.	Soil-tensiometer cup water conductance under saturated and unsaturated conditions	49
5	Dispersion coefficient values of ^{36}Cl and 2,4-D at v=7.92 cm/hr, calculated by four different approaches	51

LIST OF FIGURES

Figure		Page
1	Soil water content-suction characteristic curve of Lakeland fine sand	37
2	Calculated and measured hydraulic conductivities of Lakeland fine sand	38
3	Results of thin layer chromatograph analyses for 2,4-D on selected soil solution samples	41
4	Rate of 2,4-D adsorption on Lakeland fine sand for selected concentrations	43
5	Rate of 2,4-D adsorption on Lakeland fine sand for 6 ppm concentration	44
6	Equilibrium adsorption isotherms of 2,4-D on Lakeland fine sand with and without organic matter	45
7	Adsorption-desorption equilibrium isotherms of 2,4-D on Lakeland fine sand	47
8	Relationships of chloride and 2,4-D dispersion coefficients and pore water velocity under saturated and unsaturated flow conditions (a, b, c, d, e, and f correspond to water content, θ, 0.37, 0.30, 0.37, 0.25, and 0.37, respectively) in Lakeland fine sand	52
9	Bulk density along the sand column	54
10a	Calculated and experimental soil water content distributions for 2 cm/hr surface water flux and 0.012 cm^3/cm^3 initial soil water content	58
10b	Calculated and experimental chloride distributions for 2 cm/hr surface water flux and 0.012 cm^3/cm^3 initial soil water content	59
10c	Calculated and experimental 2,4-D soil solution content distributions for 2 cm/hr surface water flux and 0.012 cm^3/cm^3 initial soil water content	60
11a	Calculated and experimental soil water content distributions for 2 cm/hr surface water flux and 0.109 cm^3/cm^3 initial soil water content	61
11b	Calculated and experimental chloride distributions for 2 cm/hr surface water flux and 0.109 cm^3/cm^3 initial soil water content.	62

Figure		Page
11c	Calculated and experimental 2,4-D soil solution content distributions for 2 cm/hr surface water flux and 0.105 cm^3/cm^3 initial soil water content.	63
12a	Calculated and experimental soil water content distributions for 2 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water content.	64
12b	Calculated and experimental chloride distributions for 2 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water content	65
12c	Calculated and experimental 2,4-D soil solution content distributions for 2 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water content	66
13a	Experimental soil water content distributions for 4 cm/hr surface water flux and 0.012 cm^3/cm^3 initial soil water content.	67
13b	Experimental chloride distributions for 4 cm/hr surface water flux and 0.012 cm^3/cm^3 initial soil water content	68
13c	Experimental 2,4-D soil solution content distributions for 4 cm/hr surface water flux and 0.012 cm^3/cm^3 initial soil water content	69
14a	Calculated and experimental soil water content distributions for 4 cm/hr surface water flux and 0.109 cm^3/cm^3 initial soil water content.	70
14b	Calculated and experimental chloride distributions for 4 cm/hr surface water flux and 0.109 cm^3/cm^3 initial soil water content.	71
14c	Calculated and experimental 2,4-D soil solution content distributions for 4 cm/hr surface water flux and 0.109 cm^3/cm^3 initial soil water content.	72
15a	Calculated and experimental soil water content distributions for 4 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water content	73
15b	Calculated and experimental chloride distributions for 4 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water content.	74
15c	Calculated and experimental 2,4-D soil solution content distributions for 4 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water content.	75

Figure		Page
16a	Experimental soil water content distributions for 8 cm/hr surface water flux and 0.012 cm^3/cm^3 initial soil water content.	76
16b	Experimental chloride distributions for 8 cm/hr surface water flux and 0.012 cm^3/cm^3 initial soil water content.	77
16c	Experimental 2,4-D soil solution content distributions for 8 cm/hr surface water flux and 0.012 cm^3/cm^3 initial soil water content.	78
17a	Calculated and experimental soil water content distributions for 8 cm/hr surface water flux and 0.105 cm^3/cm^3 initial soil water content.	79
17b	Calculated and experimental chloride distributions for 8 cm/hr surface water flux and 0.109 cm^3/cm^3 initial soil water content.	80
17c	Calculated and experimental 2,4-D soil solution content distributions for 8 cm/hr surface water flux and 0.109 cm^3/cm^3 initial soil water content.	81
18a	Calculated and experimental soil water content distributions for 8 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water content.	82
18b	Calculated and experimental chloride distributions for 8 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water content.	83
18c	Calculated and experimental 2,4-D soil solution content distributions for 8 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water content.	84

Abstract of Dissertation Presented to the Graduate Council
of the University of Florida in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy

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December, 1974

Chairman: Dr. Robert S. Mansell
Major Department: Soil Science

The objective of this study was to investigate the effect of a wide range of water supply rates and initial soil water contents on the simultaneous transport of water and solutes, 2,4-D herbicide and chloride in Lakeland fine sand.

Using nondestructive measurements of water content and solute concentration, the simultaneous transport of ^{36}Cl-labeled sodium chloride, ^{14}C-labeled 2,4-D (2,4-dichlorophenoxyacetic acid) herbicide, and water was determined during water infiltration of laboratory columns of Lakeland fine sand under isothermal conditions. Vertical columns were prepared by uniformly packing air-dry soil into acrylic plastic cylinders of 7.6 cm diameter and 107 cm length. Two cm of an aqueous solution containing 57.9 ppm chloride and 5 ppm 2,4-D in 0.01 N $CaSO_4$ with 0.5% phenol was introduced at constant liquid flux to the top of each soil column. Immediately after the solution infiltrated the soil surface it was replaced by solute-free water (0.01 N $CaSO_4$ with 0.5% phenol) at the same flux until the water front reached the bottom of the soil column. Infiltrations of solutions and water were performed with 3 intensities (2.0, 4.0, and 8.0 cm/hr) on air dry and partially wet (0.012, 0.109, and 0.202 cm^3/cm^3

water) soil columns to evaluate the effects of initial soil-water content and water supply rates upon the simultaneous transport of water and selected solutes in Lakeland fine sand. Gamma-ray attenuation and pressure transducer tensiometers were used to precisely monitor soil-water content and water pressure distributions with time. Soil solution was extracted at selected depth intervals along the soil columns with a specially constructed device using a fritted glass porous plate and partial vacuum. Extracted samples were then analyzed for 2,4-D and chloride content with a liquid scintillation counting system. Thin layer and gas chromatography analyses of randomly selected soil water samples indicated that the herbicide did not disintegrate during transport through the soil columns.

Equilibrium adsorption-desorption isotherms for 2,4-D herbicide and Lakeland sand were characterized by Freundlich's equation. Dispersion coefficients of chloride and 2,4-D were evaluated within a range of pore-water velocities under saturated and unsaturated conditions using the miscible displacement technique during steady liquid flow through smaller columns (7.6 cm long and 7.6 cm diameter). Dispersion coefficients for both solutes were observed to increase linearly with increasing pore-water velocities within the measured range.

The depth to which chloride and 2,4-D moved for a given quantity of infiltrated water was found to depend upon the surface water flux. Increasing the water application rate resulted in an increased water content in the surface soil and in a shallower displacement of chloride and 2,4-D for equal cumulative infiltrations. For a given quantity of water infiltrated, initial soil-water content did not influence the depth of chloride or 2,4-D transport. Adsorption by the soil, caused the 2,4-D

distribution to lag behind that for chloride during experiments.

A utilized numerical mathematical solution successfully predicted experimental distributions of water and chloride during water infiltration into Lakeland fine sand. However, the solution did not adequately describe the experimental distribution of 2,4-D herbicide.

INTRODUCTION

Evapotranspiration, infiltration, redistribution and drainage processes of the soil-water-plant system provide dynamic and vital interconnecting links between rain water and ground water. The soil-water-plant system acts as an active filter against pollutants during recharge of the ground water, and also provides hydrologic buffering capacity against floods and droughts by temporary storage of infiltrating rain water. Knowledge of physicochemical behavior of the soil is needed for optimum management of these systems to provide maximum production of food, feed, and fiber and efficient disposal of waste water with minimal impairment of environmental quality.

Since water is a good solvent, soil water is invariably a solution (Vriets, 1967) of salts and dissolved gases, which move both within and with the water phase. Solutes such as cations undergo a net ionic exchange between the soil solution and the soil's exchange complex; other dissolved solutes undergo chemical precipitation and thus are removed from the solution, some volatilize and escape into the atmosphere, some may be synthesized or degraded by biological activity, and finally, some may be leached from the soil profile during periods of drainage or deep percolation.

In management of modern agricultural systems, large quantities of water-soluble chemical materials such as commercial fertilizers, herbicides, nematocides, and dolomitic limestone are frequently applied to the soil surface. Estimations of the magnitude of the water-pollution hazard posed by each specific chemical should be based on quantitative research investigations of those processes that control movement of solute from the soil surface through the root zone of the plant downward

to the underlying ground water. Development of optimum management schemes for the purpose of preventing soil and water pollution must be based upon results from field and laboratory experiments carefully designed and established to yield information capable of quantitative interpretation and comparison to theoretical models.

During the past few years considerable research effort has been directed toward investigations of miscible displacement of chemical solutes (fertilizers and herbicides) through laboratory columns of soil. Numerical mathematical techniques utilizing digital computers have been found a realistic means for solving well-posed boundary value problems which describe solute movement. In much of this work the solute was assumed to be inert with respect to the soil-water environment. In addition, most of these studies have been limited to simplified conditions of steady liquid flow in which the soil or the porous material is completely saturated with solution or has a constant unsaturated water content. Recently, Warrick et al. (1971) presented a numerical simulation technique to approximate the displacement of a noninteracting solute such as chloride during steady infiltration of water into the soil. More recently, Bresler (1973) used a numerical technique to describe the simultaneous transport of a noninteracting solute and water in unsaturated soil during unsteady infiltration.

The general objective of this study was to investigate the effect of a wide range of water supply rates and initial soil water contents upon the simultaneous transport of water and solutes, 2,4-D herbicide and chloride, in Lakeland fine sand.

LITERATURE REVIEW

In a classic study on isothermal flow of water through saturated sand in 1856, Henry Darcy observed flow velocity to be directly proportional, but in opposite direction, to the hydraulic gradient imposed across the bed of sand. Darcy's equation has been widely accepted as the basis for describing flow of liquids in saturated and unsaturated porous material. In 1950, Childs and Collis-George introduced the soil-water-diffusivity concept as a means to describe flow in water-unsaturated soils. Their theory for unsaturated water flow assumes Darcy's equation can be written as a diffusion-type water flow equation in homogeneous soils where gradients of water content rather than gradients of total potential are expressed

$$V = -D(\theta)\ \nabla\theta + K(\theta) \qquad [1]$$

where V is the water flux (cm/hr),

θ is the soil water content on a volume basis (cm^3/cm^3),

$D(\theta) = K(\theta)/C(\theta)$ is the soil water diffusivity (cm^2/hr),

$C(\theta) = \partial\theta/\partial h$ is the specific soil water storage capacity (cm^{-1}),

$K(\theta)$ is the soil hydraulic conductivity (cm/hr), and

$\nabla\theta$ is the water content gradient (cm^{-1}).

Both $D(\theta)$ and $K(\theta)$ are functions of soil water content, θ. Equation [1] can also be written in the form

$$V = -K(\theta)\ \nabla H \qquad [2]$$

where H is the hydraulic head (cm). The advantage of equation [2] over equation [1] is that equation [2] is a general form which can be used for unsaturated heterogeneous soils.

Equation [1] resembles Fick's Law of Diffusion with a concentration dependent diffusivity, except for the $K(\theta)$ term which arises from the

gravitation component of total hydraulic head. Combining equation [1] with the equation of continuity yields a "diffusion-type" equation for flow in porous media under isothermal conditions (Kirkham and Powers, 1972), which can be written in the form

$$\partial\theta/\partial t = \nabla \quad D(\theta)\ \nabla\theta - \partial K(\theta)/\partial z \qquad [3]$$

where t is the time, and z is the vertical space coordinate. The term $\partial K(\theta)/\partial z$ in equation [3] is normally referred to as the gravitational component.

The validity of equation [3] in describing the flow of water in homogeneous unsaturated soils has been demonstrated by several workers [Peck (1964), Selim et al. (1970), Youngs (1957), among others]. For a review and detailed derivation of the laws governing soil water movement, the reader may refer to an extensive review article by Gardner (1960) in which he cites over 300 references.

During transient soil-water content flow when changes in soil water content occur, solutes tend to move simultaneously with water through the soil. An exact analytical mathematical solution for the transient flow case is not available in the literature since such a solution would require the simultaneous solution of two parabolic nonlinear partial differential equations. Also complications stemming from inability to mathematically describe the geometry of the soil pore space and complex biological and physicochemical interactions between solutes and the soil matrix do not permit development of a completely heuristic theory of miscible displacement phenomena. However, Nielsen et al. (1972) wrote the following expression for the flux of solutes J_s during miscible displacement of a solute through uniform soil with uniform water content and undergoing steady liquid flow:

$$J_s = vC - D_s \partial C/\partial x \qquad [4]$$

where C is the concentration (μg solute per ml of soil water) of the solute in the soil water, $v = V/\theta$ is the average interstitial or pore water flow velocity (soil water flux or Darcy velocity divided by the soil water content), D_s an apparent diffusion (or dispersion) coefficient, and x the distance. They mentioned that both terms on the right hand side of this equation are only approximations. In as much as the actual spacial distribution of microscopic velocity within pores and pore sequences is not constant nor can it be described as an explicit mathematical function, the use of a macroscopic average offers potential error. Moreover, the microscopic concentrations of solute varies within pores and pore sequences and thus give rise to an additional uncertainty due to the use of the term vC to describe solute moving with the water. Regardless of the potential shortcomings of equation [4], it has been found particularly useful in description and simulation of solute leaching studies. For a uniform soil with constant uniform water content, combining equation [4] with the equation of mass conservation and including a sink-source term for solute-soil interaction yields the equation

$$\partial C/\partial t = \partial/\partial x \, (D_s \, \partial C/\partial x) - \partial/\partial x \, (vC) + f_n(C, x, t)$$

$$n = 1, 2, 3, \ldots \qquad [5]$$

where t is time and f_n are terms which account for losses and gains in solute concentration attributable to chemical precipitation, ionic exchange, degradation, sorption-desorption, etc. This equation, subject to specific initial and boundary conditions, offers an analytical means of examining numerous boundary value problems (Nielsen and Biggar, 1962; Nielsen and Jackson, 1969) of miscible displacement of solutes.

Scheidegger (1954) and Day (1956) used statistical theory to describe

miscible displacement of an inert solute within porous material but they disregarded the actual microscopic flow paths or the physical properties of the fluid. They considered a hydrodynamic mechanism which does not involve molecular diffusion to cause transport of solute through the porous media. Displacement was treated as a random-walk process consisting of successive, statistically-independent straight steps taken in equal small time intervals. Similar analyses (de Josselin de Jong, 1958, Saffman, 1960, Rifai et al., 1956) including direction of paths, pore lengths and diffusion have led to the following equation which is that derived by Danckwerts (1953)

$$\partial C/\partial t = D_s \partial^2 C/\partial x^2 \qquad [6]$$

where D_s is a dispersion coefficient. The movement of solute is considered random because the pore-water velocity will fluctuate irregularly about an average velocity. Equation [6] and similar equations written for multi-dimensional cases have been used to describe dispersion in relatively inert soil materials saturated with water.

Most reported studies of dispersion and adsorption of chemicals are for chromatographic columns or ion exchange resin beds under steady water flow conditions. Lapidus and Amundson (1952) presented an analytical solution for a dispersion model with linear equilibrium and finite rate of adsorption. Their solutions are valid for infinitely long columns and for steady flow conditions. Brenner (1962) later presented a solution for dispersion in finite columns under steady flow conditions. Brenner improved the model postulated by Lapidus and Amundson (1952) by incorporating a more realistic solute flux boundary condition at the soil surface. Hashimoto, Deshpande, and Thomas (1964) presented a different solution for the same problem considered by Brenner (1962). In their solution,

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they included a "retardation factor" for solute movement based on linear adsorption isotherms at equilibrium. Lindstrom, Hague, Freed, and Boersma (1967) extended this work for semi-infinite soil columns with a "flux-plug-type" input at the soil surface. Cleary and Adrian (1973) solved the problem of solute movement in soil columns of finite length and under steady water flow conditions. Their solution is based on a simplified constant concentration (first order) boundary conditions at the soil surface.

In the previously mentioned papers, solute movement is considered under steady water flow conditions. Furthermore, these models assumed either no interaction between the solute and the soil particles, or a linear relationship between the concentration of solute in the soil solution and the amount adsorbed or desorbed on the soil surface at equilibrium. The problem of solute movement with nonlinear adsorption relationships are more complex since the solute flow equation becomes nonlinear. Because of this nonlinearity, published solutions of the partial differential equation for solute flow are based on numerical methods rather than analytic methods. Lai and Jurinak (1972a) used explicit finite difference methods (Richmeyer and Morton, 1967) in solving the solute flow problem for 4 nonlinear adsorption relationships. The nonlinear relations of the adsorption curves were concave and convex which are sometimes referred to as favorable and unfavorable exchange isotherms, respectively (Reiniger and Bolt, 1972). Gupta and Greenkorn (1973) considered a bilinear adsorption relation where a second order reaction between the solute in the soil solution and that adsorbed was considered. Their numerical method of solution is based upon an implicit-explicit finite difference technique.

Martin and Synge (1941), a Nobel Prize winning paper, considered that development of a chromatogram to be closely analogous in its mode of operation to distillation and extraction fractionating columns and developed the theory of chromatography. They proposed the concept of 'theoretical plates'. From that beginning, the theory of chromatography has developed into a very refined technique in studying movement of chemical in adsorbent beds for chemical engineers and civil engineers. Giddings (1959) started the development of generalized nonequilibrium theory of chromatography. He stated that the limit of theoretical accuracy was to be determined by how closely the structural and adsorptive features of the column could be categorized and described. In 1965 he concluded that the ganarelized nonequilibrium theory has led to the narrowest gap found between theory and experiment and it accounted for an error of about 10%.

The experimental data of Kay and Elrick (1967) and Davidson and Chang (1972) shows a non-singular adsorption-desorption relationship for several chemicals. Also, their results show that equilibrium adsorption may not exist over a wide range of soil-water flow rates. Davidson, Mansell, and Baker (1972), assuming a constant infiltration rate as well as a constant soil-water content in the transmission zone, calculated the effect of the non-singularity of the first order kinetic adsorption-desorption process upon the herbicide distribution within a soil profile. They concluded that the non-singularity tends to increase the length of soil profile over which the distribution occurs as well as decreases the maximum herbicide solution concentration. Also, they stated that the use of the distribution coefficient for herbicide in solution and adsorbed phases to estimate the position of the leading herbicide

front during infiltration is only suitable for equilibrium adsorption and when herbicide concentrations in the adsorbed and solution phases are linearly related at equilibrium.

Jyothi* (1971) studied the miscible displacement of 2,4-D herbicide during steady irrigation to columns of initially dry Lakeland fine sand. He assumed that the transport of solute results primarily by mass flow and adsorption occurs as a first order reaction. The adsorption isotherm at equilibrium was experimentally determined to be linear. He concluded that the herbicide moved readily through the soil and most of it was recovered within two pore volumes of effluent after the wetting front had reached the length of the 30 cm column. A limitation of his work is that the assumption of a constant liquid flux at the boundary would not provide a constant soil water content (which he assumed) during the early stages of introducing the 2,4-D solute into the air dry Lakeland fine sand. Measurements of water content were not performed.

Taylor (1953), Scheidegger (1954), Bear and Todd (1960), and others have studied the relationship between apparent diffusion coefficient and flow velocity. In the final analysis, all relations studied were empirical and particularly inadequate for miscible displacement occurring in water-unsaturated media where continuous air and liquid phases coexistad. Harleman and Rumer (1962) suggested the relation:

$$D_s = D_o + a\, v^b \qquad [7]$$

where D_o is the molecular diffusion coefficient corrected for the conditions of the soil, v the average pore water velocity, and a and b are empirical constants characterizing the porous media. Kirda et al (1973)

* Jyothi, V. 1971. Miscible displacement of 2,4-D herbicide during constant liquid flow velocity into initially dry soil. Published Ph.D. dissertation, University of Florida, Gainesville, Florida.

reported that S_0 and b are within the range of 4.3×10^{-4} (cm²/min) and 1.355, respectively, for the chloride movement under transient water flow conditions in a loam soil. Davidson et al. (1972) used equation [7], with b=1 and S_0=0.01, to study the movement of a herbicide through soil under a constant infiltration rate and to evaluate the effect of adsorption-desorption upon herbicide distributions within the soil profile.

During recent years the more realistic problem of solute movement under transient or unsteady water flow conditions has been the focus for development of mathematical models. Under field conditions soil water flow is normally unsteady, thus the problem becomes one of simultaneous solute and water movement rather than solute movement only. Bresler and Hanks (1969) presented a numerical method for non-interacting salt movement simultaneously with water for vertical infiltration and evaporation.

Warrick et al. (1971) assuming a steady infiltration rate, studied the transfer of surface applied water and solute downward through unsaturated homogeneous soil. Chloride ion was used as the solute and the interaction of the solute and soil matrix was ignored as a first approximation. Their method of solution was analytical and exact for dissipation of a finite solute "slug" moving at a constant velocity through an infinite medium. In a field experiment, they applied $CaCl_2$ solution and then followed the solution immediately with solute-free water. They found that the downward advance of the front of applied chloride was nearly independent of the initial soil-water content but highly dependent upon the water content maintained at the soil surface during steady infiltration.

Kirda et al. (1973) studied two cases of miscible displacement of

chloride through soil columns during water infiltration 1) where chloride was initially spread on the soil surface; and 2) where chloride was initially mixed with the soil. Chloride was applied as $CaCl_2$ labeled with ^{36}Cl. Activity of the ^{36}Cl was obtained by scanning the side of the soil columns with GM counter. In conjunction with the chloride activity measurements, gamma-ray attenuation measurements of soil water content distribution were monitored during simultaneous flow of chloride and water. They found that the initial soil water content did not influence the depth to which chloride penetrated the soil for a given quantity of water infiltrated at the soil surface. In addition, a numerical procedure based on an implicit-explicit technique for solving simultaneous equations describing vertical water flow and solute miscible displacement were used to obtain the calculated data. They concluded that experimental and calculated chloride distributions were in good agreement.

Bresler (1973) presented a numerical approach using the Crank-Nicholson method (Crank, 1956) for simulating the transport of a non-interacting solute in the soil during nonsteady infiltration, redistribution and evaporation of water under isothermal conditions. The results were compared with simplified analytical solutions and with experimental field infiltration data reported by Warrick et al. (1971). These comparisons indicated that the theory as well as the numerical method are reliable and can be used with confidence.

Skopp and Warrick (1974) presented a two-phase model for miscible displacement of reactive solutes in soils. They assumed that the flow regime of the soil can be divided into distinct mobile and stationary phases. In this model, solute transfer through the mobile phase was

assumed to be diffusion-limited and occurs normal to the mobile-stationary interface. The model is unique in that a specific rate law is not assumed, and it can be applied for saturated and unsaturated flow, but the solution is exact. The primary disadvantage of this model is that it oversimplifies the soil porous system. They compared their theoretical results with the experimental work of Lai and Jurinak (1972b) and Davidson and Cheng (1972). They concluded that the agreement between the theoretical and experimental results was good for the displacement of calcium by magnesium at both high and low fluxes (2.97 and 0.198 cm/hr), however, the fit was not good in the case of the displacement of picloram using the data of Davidson and Cheng (1972). Nonsingle-valued adsorption and desorption (van Genuchten et al., 1974) was given as an explanation for the poor fit between theorical and experimental data for picloram.

This literature review indicates that very few investigators have considered solute transport under transient water flow conditions, and no known published research considers simultaneous transfer of an interacting solute and water under transient, water-unsaturated flow. The objectives of this study were two-fold:

1. To investigate the effect of 3 different supply rates of water [2.0, 4.0, and 8.0 cm/h] at the soil surface,

and 2. The effect of 3 initial soil-water content [0.012 (air-dry), 0.109, and 0.202 cm^3/cm^3],

upon the simultaneous transport of water, chloride, and interacting 2,4-D herbicide in Lakeland fine sand during water infiltration at the soil surface.

THEORY

Water and Solute Flow Equations

Consider a homogeneous and uniformly packed soil column with initial water content θ_i. For isothermal vertical flow of water into soil, the equation describing this flow process is:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[D(\theta)\ \frac{\partial \theta}{\partial z}\right] - \frac{\partial K(\theta)}{\partial z} \qquad [8]$$

where θ is the volumetric soil water content (cm^3/cm^3), z the distance (cm) measured positively downward, $K(\theta)$ the hydraulic conductivity (cm/hr), and $D(\theta)$ the soil water diffusivity (cm^2/hr). Equation [8] can be easily derived using the equation of continuity and Darcy's Law assuming its validity for unsaturated flow (Kirkham and Powers, 1972) and there exists a unique relation between water content and pressure (such is the case for a strictly wetting or drying case).

The one-dimensional miscible displacement equation applicable to non-interacting solute transport problems under transient water flow conditions is

$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z}\left[\theta\, D_s\, \frac{\partial C}{\partial z}\right] - \frac{\partial(VC)}{\partial z} \qquad [9]$$

where C = solute concentration in solution ($\mu g/cm^3$)

D_s = solute diffusion-dispersion coefficient (apparent diffusion coefficient), (cm^2/hr). Its value depends on the average water flow velocity and the soil water content (Olsgar and Nielsen, 1967).

V = Darcy's water flux (cm/h).

If D_s is assumed constant, equation [9] may be simplified to

$$\frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z}\left[\frac{V}{\theta} - \frac{D_s}{\theta}\ \frac{\partial \theta}{\partial z}\right] \qquad [10]$$

Equation [10] can be written, using the relation

$$D(\theta) = K(\theta)\ \frac{dh}{d\theta} \qquad [11]$$

where $\frac{d\theta}{dh}$ is the slope at any given point on the soil characteristic curve, as the form

$$\frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial z^2} - \frac{1}{\theta} \frac{\partial C}{\partial z} [K(\theta) - \{D(\theta) + D_s\} \frac{\partial \theta}{\partial z}] \quad [12]$$

In case D_s is allowed to vary as a function of water flow velocity and/or soil water content, equation [9] can be written in the form

$$\frac{\partial C}{\partial t} = D_s^* \frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z} [\frac{V}{\theta} - \frac{D_s^*}{\theta} \frac{\partial \theta}{\partial z} - \frac{\partial D_s^*}{\partial z}] \quad [13]$$

Using equation [11], equation [13] can be rewritten as

$$\frac{\partial C}{\partial t} = D_s^* \frac{\partial^2 C}{\partial z^2} - \frac{1}{\theta} \frac{\partial C}{\partial z} [K(\theta) - \{D(\theta) - D_s^*\} \frac{\partial \theta}{\partial z} - \theta \frac{\partial D_s^*}{\partial z}] \quad [14]$$

For an interacting solute, equation [9] can be written in the form

$$\theta \frac{\partial C}{\partial t} + \frac{\partial S}{\partial t} = \theta D_s^* \frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z} [V - D_s^* \frac{\partial \theta}{\partial z} - \frac{\partial D_s^*}{\partial z}] \quad [15]$$

in which we added an adsorption-desorption term, S($\mu g/cm^3$ of soil), solute concentration in adsorped phase, to account for the kinetics of the adsorbed solute. Lapidus and Amundson (1952) proposed the general relation for adsorption-desorption of the form

$$\frac{\partial S}{\partial t} = f(C,S) \quad [16]$$

where f(C,S) can be any function of C and S. For mass transfer rate of the adsorbed solute, Davidson and McDougal (1973) used the equation

$$\frac{\partial S}{\partial t} = \frac{\theta}{\rho} k_a C - k_d S \quad [17]$$

where t is time (hrs), θ the soil-water content (cm^3/cm^3), k_a and k_d are the adsorption and desorption rate constants (hr^{-1}), and ρ the bulk density of the soil system (g/cm^3), to predict the movement of three herbicides through soil. They concluded that the use of equation [17] as a kinetic adsorption model in a convective transport equation did not adequately predict the shape of the effluent concentration distribution at high pore-water velocities. It should be pointed out that equation [17] assumes the adsorption process to be completely reversible and that a linear relation exists between S and C at equilibrium. Van Genuchten

et al. (1974) compared experimental and predicted effluent concentration distribution of picloram through soil. Predictions were made with a simulation model using two kinetic rate equations and an equilibrium Freundlich equation. They found that, at high pore-water velocities, the kinetic adsorption models based on equations presented by Lindstrom et al. (1971) and Oddson et al. (1970) were inadequate to predict the picloram movement through soil provided the nonsingle-valued character of the adsorption-desorption process was included in the calculations. However, with an empirical model, based on the assumption that equilibrium existed during displacement, a reasonable fit between data and calculated effluent curves was obtained for all pore-water velocities ranged from 0.59 to 6.1 cm/hr.

Based upon the most recent evalnation of various adsorption-desorption models made by van Genuchten et al. (1974), Sawanson and Dutt (1973) and others, the author suggests that the instantaneous equilibrium Fruandlich relations offers much potential.

$$S = k_a C^{1/n} \quad \text{for adsorption} \qquad [18a]$$

$$S' = k_d C'^{1/n'} \quad \text{for desorption} \qquad [18b]$$

where k_a and k_d are the adsorption and desorption distribution coefficients and n and n' are constant that vary with the solute and adsorbent, to be used in equation [15] to account for the adsorption-desorption of solute during transient flow of water through soil. The prime (') in equation [18b] denotes desorption. Van Genuchten et al. (1974) proposed the formula

$$k_d = k_a C_{max}^{(1/n - 1/n')} \qquad [19]$$

where C_{max} is the maximum solute concentration that existed at a given location before desorption, from which k_d can be obtained. Note that k_d

is not constant, but a function of C_{max}, however, van Genuchten et al (1974) has shown that n' was inversely related to C_{max}, but could be assumed constant without introducing a serious error

Finite Difference Approximation for Water and Solute Flow Equations

The water flow equation [8], and the solute flow equation [9] are nonlinear second-order parabolic partial and differential equations Because of nonlinearity these equations are difficult to solve because $K(\theta)$, $\frac{dh}{d\theta}$, h, and $D(\theta)$ are all functions of θ and sometimes are hysteretic functions To solve the equations these functions must be determined by empirical or other means Because exact solutions of such nonlinear equations are very difficult and sometimes impossible to obtain, numerical methods are frequently used to provide solutions (Remson et al., 1971) to individual boundary value problems

Numerical Solution of Water and Solute Equations

The first step in obtaining a numerical solution for simultaneous differential equations [8] and [9] is to express them as finite difference approximations (Richmeyer and Morton, 1967) Three main types of methods commonly used to provide finite difference approximations are fully implicit, fully explicit, and implicit-explicit methods. The Crank-Nicholson method (implicit-explicit method) provides a number of advantages over the fully explicit and fully implicit methods (McCracken and Dorn, 1964) Using this method, the finite difference approximation of the water flow equation [8] is

$$\frac{\theta_{i,j+1} - \theta_{i,j}}{\Delta t} = \frac{D(\theta_{i+\frac{1}{2},j+\frac{1}{2}}) \left[\theta_{i+1,j+1} - \theta_{i,j+1}\right]}{2(\Delta z)^2} - \frac{D(\theta_{i-\frac{1}{2},j+\frac{1}{2}}) \left[\theta_{i,j+1} - \theta_{i-1,j+1}\right]}{2(\Delta z)^2}$$

$$\frac{+D(\theta_{\ell+\frac{1}{2},j+\frac{1}{2}})\ [\theta_{\ell+1,j} - \theta_{\ell,j}]}{2(\Delta z)^2}$$

$$\frac{-D(\theta_{\ell-\frac{1}{2},j+\frac{1}{2}})\ [\theta_{\ell,j} - \theta_{\ell-1,j}]}{2(\Delta z)^2}$$

$$\frac{-K(\theta_{\ell+1,j+\frac{1}{2}}) - K(\theta_{\ell-1,j+\frac{1}{2}})}{2\Delta z} \qquad [20]$$

Similarly, the finite difference approximation for the inert solute flow equation [12], where D_s is assumed to be constant, is

$$\frac{C_{\ell,j+1} - C_{\ell,j}}{\Delta t} = \frac{D_s\ [C_{\ell+1,j+1} - 2C_{\ell,j+1} + C_{\ell-1,j+1} + C_{\ell+1,j} - C_{\ell,j} + C_{\ell-1,j}]}{2(\Delta z)^2}$$

$$- \frac{K(\theta_{\ell,j+1}) - [D(\theta_{\ell,j+1}) - D_s]}{\theta_{\ell,j+1}\ \Delta z} \cdot \frac{\theta_{\ell+1,j+1} - \theta_{\ell,j+1}}{\theta_{\ell,j+1}\ \Delta z}$$

$$\frac{C_{\ell+1,j} - C_{\ell,j}}{\Delta z} \qquad [21]$$

The method of solution is a numerical one in which $C(z,t)$ and $\theta(z,t)$ are obtained at incremental time steps, Δt, and incremental distances, Δz, in the soil system. Incremental time steps and distances are denoted by (ℓ,j) where

$$z = \ell\Delta z \qquad t = j\Delta t$$

where $\ell = 1, 2, 3, \ldots$, and $j = 1, 2, 3, \ldots$, and the values of $C(z,t)$ and $\theta(z,t)$ at any point (ℓ,j) are denoted by $C_{\ell,j}$ and $\theta_{\ell,j}$, respectively,

$$C(z,t) = C(\ell\Delta z,\ j\Delta t) = C_{\ell,j} \qquad [22a]$$

$$\theta(z,t) = \theta(\ell\Delta z,\ j\Delta t) = \theta_{\ell,j} \qquad [22b]$$

Using a digital computer, equation [20] can be solved for the soil water content $\theta_{\ell,j+1}$ at time step $j+1$, where $\theta_{\ell,j}$ is known from the initial condition (at time step 1) of the problem. Using the value of $\theta_{\ell,j+1}$ as computed from equation [20] as well as $C_{\ell,j}$ and $\theta_{\ell,j}$ from the initial conditions, equation [21] can be solved simultaneously for noninteracting

solute concentrations $C_{i,n+1}$. Repeating the solutions of equations [20] and [21] alternately would provide the solute concentration and soil water content at a specific time as desired.

Initial and Boundary Conditions

To be able to predict the soil water content and solute concentration for a specific boundary value problem, equations [20] and [21] must be solved for a given set of initial and boundary conditions. Before applying a solute such as a fertilizer, herbicide, or nematocide and irrigation water to the soil surface the initial distributions of θ and C throughout the soil profile determine the initial conditions.

At the soil surface a time dependent flux boundary condition for water can be written as

$$\text{at } z = 0, \quad V_0(t) = -D(\theta)\frac{\partial \theta}{\partial z} + K(\theta), \quad t>0 \qquad [23]$$

This condition applies when water flow occurs into the soil during infiltration with rainfall or sprinkler irrigation intensity which varies as some function, V(t), of time. Note that in this study we assumed $V_0(t)$ to be constant during a given experiment. The flux boundary conditions of solute can be written as

$$\text{at } z = 0, \quad -D_s\theta\frac{\partial C}{\partial z} + VC = VC_0 \quad 0<t\leq t^* \qquad [24]$$

$$\text{and} \quad -D_s\theta\frac{\partial C}{\partial z} + VC = 0, \quad t>t^* \qquad [25]$$

where C_0 being equal to the maximum solubility of the solute in water. These boundary conditions allow for application of salt solution until time $t = t^*$, where application of solute is discontinued. Equations [24] and [25] take into account mass flow and hydrodynamic dispersion.

For the lower boundary located at some distance below the soil surface (in our laboratory columns study, the boundary is located below 100 cm from the soil surface) the boundary condition of water for a semi-infinite

soil column is

$$\frac{\partial \theta}{\partial z} = 0, \quad \text{as } z \to \infty, \quad t > 0 \qquad [26]$$

which implies that the soil-water content is constant and the moving water front has not reached the bottom of the soil column.

The initial conditions are uniform solute and water content distributions at time, t = 0. They can be written in the form

$$C = C_i \quad 0 < z < \infty \quad t=0 \qquad [27]$$

$$\theta = \theta_i \quad 0 < z < \infty \quad t=0 \qquad [28]$$

where C_i and θ_i are the initial salt concentrations and water content, respectively.

FORTRAN IV computer program has been developed by Selim and Mansell (1974) for solving the nonlinear partial differential equations of solute and water given previously by equations [8] and [12]. The method of solution is a numerical one which utilizes the explicit-implicit finite difference technique given by equations [20] and [21]. A more general solution for solute and water flow in a homogeneous one-dimensional soil has been obtained by Selim, Mansell, and Elzeftawy (1974). Their solution included the dispersion coefficient as a function of pore-water velocity, nonuniform initial water and solute content, variable surface water flux, and adsorption-desorption of solute as a function of solute concentration. Selim et al. (1974) computer program was used in this study to obtain the calculated distributions of water content, chloride, and interacting 2,4-D herbicide for the following initial and boundary conditions:

$$C = C_i = 0 \quad 0 < z < \infty \quad t=0 \qquad [29]$$

$$\theta = \theta_i = 0.012,\ 0.109,\ 0.202 \quad 0 < z < \infty \quad t=0 \qquad [30]$$

and at z=0 V = 2.0, 4.0, 8.0 cm/hr

C_o = 50 ppm for Cl

C_o = 5 ppm for 2,4-D $\quad 0 < t \leq t^* = 1$ [31]

C_o = 0.0 ppm for Cl and 2,4-D $\quad t > 1$ [32]

For the calculation of the 2,4-D distribution during infiltration, the rate of adsorption-desorption $\frac{\partial s}{\partial t}$ of equation [15] was obtained by use of the adsorption isotherm determined in this study

MATERIALS AND METHODS

Soil Sampling

Lakeland fine sand, a member of the thermic coated family of Typic Quartzipsamments*, was the soil material used in this study. Bulk samples of surface soil, 0-15 cm, were collected from a field located at the Agricultural Research and Education Center near Quincy, Florida. These samples were air-dried and then passed through a 2 mm sieve. The dried soil was then stored in air-tight polyethylene bags in the laboratory and was later used to pack soil columns. Undisturbed soil core samples (3 inches diameter and 3 inches long) were also collected from several depths at the same site as described by Elzeftawy and Mansell (1975). The cores were later used to determine the functions K(θ) and θ(h).

Soil Analyses

Particle size distribution of the surface soil was determined using the dry sieve method (Day, 1965) for fractions larger than 0.053 mm in diameter and the hydrometer method (Bouyoucos, 1962) was used for fractions less than 0.053 mm. The soil was pretreated with 30% H_2O_2 to remove the organic matter.

Organic matter content was determined by a procedure described by Walkley and Black (1934).

Cation exchange capacity of the soil was determined by weighing ten grams of oven-dry soil sample which was previously saturated with aqueous 1.0 N $MgCl_2$ solution. The sample was centrifuged and washed with ethanol until free from Cl^- anion. Using aqueous 1.0 N NH_4Cl solution, the exchangeable Mg^{++} was displaced and its concentration was measured by atomic adsorption spectroscopy (Perkin-Elmer model 303).

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* Soil Taxonomy of the National Cooperative Soil Survey, Soil Conservation Service, U. S. D. A., Washington, D. C., December, 1970.

The undisturbed soil core samples were used to obtain the soil water content-pressure characteristic curve, $\theta(h)$, bulk density, ρ, and the hydraulic conductivity-water content relationship, $K(\theta)$, with procedures as described by Elzeftawy and Mansell (1975)

Physical Set-up of Soil Column Flow System

Soil columns used in this laboratory study were contained in lucite plastic cylinders with 7.6 cm in diameter and 107 cm long, giving a cross-sectional area of 45.5 cm^2. Fritted glass porous discs (coarse porosity) with air entry suction head of 97 cm housed in plastic end-plates were bolted to the top and the bottom of the plastic cylinder for each soil column. The fritted discs were firmly placed in contact with the soil in the cylinder. A very small liquid reservoir volume of 6.95 ml was located behind each porous disc. The volume of these reservoirs was considered negligible under rapid flow conditions in comparison to the pore volume of the soil column. Two inlet ports were provided directly at the reservoir behind the porous disc of the top end-plate for introducing or flushing the solute and water from the liquid reservoir. The bottom end-plate of the cylinder was fused permanently with plastic solvent on the periphery of a 4 cm long cylinder with 9.6 cm in diameter to provide a base for the soil column. One outlet was also provided directly at the reservoir behind the porous disc of the bottom end-plate for draining the soil solution or as an air vent

Matching holes of 1.25 cm in diameter were drilled at 2.5, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, and 90 cm deep from the cylinder top, along vertical lines drawn parallel to the cylindrical axis of the column upon two directly opposite walls. Matching holes on one side of the column were used to install tensiometer bulbs (medium porosity with 180 cm

air entry suction head) for measurements of soil water suction and holes on the opposite side were used to extract small volumes of soil solution for determinations of solute concentration.

To satisfy the flux boundary condition of flow at the top of the soil column the inlet port of the fritted glass disc provided for introducing solute or solute-free water, was connected to a constant head graduated burette (Nielsen et al., 1962) by means of 2 mm I.D. flexible nylon tubing. This burette served as a Marriotte device to provide measurable volumes of water flow delivered at a constant hydraulic head. A positive displacement pump (Model 130, Instrumentation Specialties Company, Lincoln, Nebraska) was placed along the nylon tubing connecting burette and the inlet port to provide a means of constant flux boundary condition at the top of the soil column.

The sampling device for extracting soil solution samples consisted of a small, medium porosity fritted glass plate in contact with the soil and a septum to facilitate drawing the samples with a hypodermic needle was operated under an applied suction of about 1750 cm of water for a period of 30 seconds at the time of sampling using a vacuum pump (Little Giant Model 13152, Gelman Instrument Company). The purpose of using high applied suction, which exceeds the air entry value of the porous plate of the sampling device, was to obtain soil solution samples in a very short period of time from the immediate vicinity of the porous plate during the infiltration of water through Lakeland fine sand. Only one sampler device was used to sequentially sample all 13 soil depths during the experiments. The physical set-up of this sampling device is described in detail by Jyothi* (1971).

* Jyothi, V. 1971. Miscible displacement of 2,4-D herbicide during constant liquid flow velocity into initially dry soil. Published Ph.D. dissertation, University of Florida, Gainesville, Florida, 32611.

Preparation of the Flow Column

The column was first assembled without tensiometers and solution sampling devices in place. Instead rubber septums with and without short lengths of 1.5 mm inside diameter glass tubing placed in holes bored in their center were fitted tightly into the 1.25 cm holes in the acrylic plastic wall of the column container. A cylindrical column extension with the same cross section as the column and 15 cm long was added to the top of the column. A long nylon tube with a funnel at the top was inserted into the upright column and sand was poured slowly into the nylon tube until the level of the air-dry sand stood in the funnel. Packing of the column with soil was achieved by raising the nylon tube slowly and at the same time moving it back and forth across the soil in the column while the level of soil in the funnell was maintained constant. No attempt was made to compact the soil during the filling operation. Once the column and extension were filled with soil the entire unit was placed in position to be scanned vertically with a gamma ray attenuation system to determine soil water content. Prior to infiltration of the column surface with water the septums were removed very gently and replaced by tensiometers which were connected to a pressure transducer water pressure sensing and monitoring system. Then, the column was tapped gently with a rubber mallet until the desired uniform bulk density was obtained. The extension was removed and the top porous plate was water-saturated and placed to apply the solute and water to the upper soil column surface.

To obtain initial soil water contents larger than air-dry values, 0.01 N $CaSO_4$ with 0.5% phenol (solute-free water) was applied under a constant pressure head through the fritted glass head plate to the top

of the soil column using the Mariotte-type burette. After infiltration of the applied solute-free water, it was allowed to redistribute to obtain a fairly uniform water content distribution before proceeding with the miscible displacement experiment. The gamma ray system was used to check the uniformity of the initial soil-water content with depth in the soil column.

Water Content and Bulk Density Measurements

A gamma ray attenuation method of nondestructive measurement of volumetric water content and bulk density of laboratory soil columns was used. The gamma system for measuring water contents and the principle involved are well documented [Ferguson and Gardner (1962), Gurr (1962), and Davidson et al (1963)]. The theory of measurement of water content with gamma radiation requires that only mono-energetic radiation be used. Simultaneous measurements of soil bulk density, ρ, and the volumetric water content, θ, may also be performed with gamma attenuation in columns of moist soil by the method of Gardner et al. (1972) using two collimated beams of mono-energetic gamma rays from ^{241}Am and ^{137}Cs by moving the soil column from one beam to the other.

A Lambert-Beer type attenuation equation for each gamma energy, 60 keV (^{241}Am) and 662 keV (^{137}Cs) permit determination of ρ and θ in terms of mass attenuation coefficients of water and dry soil, soil thickness, and the attenuation for each energy. These two attenuation equations (Corey et al, 1971) can be solved simultaneously for ρ and θ if the measured intensities of the two gamma rays are independent. The physical consideration of a dual-energy beam suggest a single detector, thus requiring some means for differentation of the intensities for the two gamma energies (Mansell et al., 1973). This separation procedure must

include corrections before the attenuation equations are simultaneously solved, that is, the equations must be linearized by correcting the two intensities for independance due to mixing of the 60 and 662 keV photons.

The mass absorption coefficients for 60 and 662 keV gamma radiation of the soil material and water were determined from attenuation measurements of the intensities of a collimated beam of rays from successive thickness of absorber material in plastic containers as described by Mansell et al. (1973).

The experimental system used in this study to determine soil water content and the bulk density, separately (using a single energy source of ^{137}Cs) or simultaneously (using a dual-energy source of ^{241}Am and ^{137}Cs), is described by Mansell et al. (1973) except that a spectrum stabilizer was added between the linear amplifier and pulse-height analyzer. The advantages of installing the stabilizer (Canberra model 1720, Canberra Industries, Meriden, Connecticut) are to provide fast and accurate corrections for gain shift occurring as large as -50% to +100%, insure drift free data acquisition over indefinitely long collection times, and compensate for the baseline shift which occurs in most amplifiers at high count rates. This stabilizer which, has a wide range of operating temperature (0 to 50°C) was used with the setting 0.25, 0.25, and 662, respectively, for the window width, spacing, and peak position for all the soil water content and bulk density measurements.

All calculations for obtaining the soil water content or the bulk density values were done using a programmable calculator (HP Model 9100 B calculator, Hewlett-Packard Company, Loveland, Colorado). The program is given in the appendix.

Soil Water Pressure Measurement

Klute and Peters (1962) and Watson (1965) previously reported the satisfactory use of a pressure transducer for soil water pressure measurements requiring rapid response with minimum transfer of water between the soil-water and the measuring systems.

Fritted glass porous cups (medium porosity) used for this study reported here as tensiometers were 0.85 cm in diameter with an air entry suction head of approximately 180 cm of water. Tensiometers were installed at 13 positions using septums and were saturated with boiled, deionized, distilled water. All tensiometers were connected with 1/16 inch O.D. nylon tubing to a single pressure transducer (Validyne Model DP15TL, Validyne Engineering Corporation, Northridge, California) by way of a common rotary switching valve (Scanivalve Model W060I/1P-24 T). The output signal of the pressure transducer was measured by a Validyne carrier demodulator (Model CD 23) and continuously recorded on a strip chart recorder (Rustrak model 400, Gulton Industries, Inc., Manchester, New Hampshire).

A constant head water column was used as a standard to calibrate the transducer at +15, 0, -15, -20, -35, -60, -80, and -125 cm pressure head. The ratio of signal voltage to differential pressure used for this study was 1mV/cm of water pressure head.

The response time-constant of the tensiometer-transducer system when the flow system was water-saturated was 0.1 to 0.3 seconds but the response became quite large ($\leq$ 15 seconds) when the flow system was in an unsaturated condition. Rapid decrease of hydraulic conductivity of the soil with decreasing water content caused an increase in the time required for the transmission of water through the porous medium to or from the tensiometer.

Richards (1949) defined the tensiometer conductance, k, as the volume of water passing through the tensiometer cup per unit of time per unit of pressure difference. For a given time and pressure difference the cup conductance depends primarily on the area of contact with soil and the pore size of its porous material. Also, he defined the gauge sensitivity, s, as the pressure change per unit volume of displacement. Watson (1965) stated that the gauge sensitivity, for the equipment under discussion, could more precisely be described as transducer sensitivity. The response time-constant is related to the tensiometer cup conductance, k, and the gauge sensitivity, s, according to Richards (1949), by the equation:

$$\tau = 1/ks \qquad [33]$$

where τ is the response time-coustant (sec.), k the tensiometer conductance ($cm^3/sec/atm$), and s the gauge sensitivity (atm/cm^3).

Since the manufacturer specified that the pressure transducer, used throughout this study, has a volumetric displacement of $4.92 \times 10^{-3} cm^3$, then, for a maximum pressure of 350 cm of water and gauge sensitivity value of $7.1 \times 10^{6}\ cm^{-3}$, it can be seen that the tensiometer cup conductance might be easily calculated from equation [8] for a specific response time-constant.

Preparation and Analysis of Solute

^{14}C-labeled 2,4-D herbicide and ^{36}Cl-labeled NaCl aqueous solutions were used throughout this study for displacement and adsorption laboratory experiments through Lakeland fine sand columns. The herbicide behaves as an interacting solute and Cl behaves as an inert solute in this soil. The ^{14}C-labeled 2,4-D herbicide was purchased from ICN Isotope and Nuclear Corp., Irvine, California. The manufacturer specified that the chemical

had a specific radioactivity of 0.46 mCi/mM at the time of shipping. A 2,4-dichlorophenoxyacetic acid capsule containing 26.1 mg (10^3µCi) of powder was emptied into 100 ml of deionized-distilled water to give a concentration of 261 ppm. The solution was stirred thoroughly and stored in a refrigerator at 4°C. The ^{36}Cl-labeled NaCl had a specific activity of 2.2 µCi/mg, at the time of shipping from the manufacturer, was purchased from Amersham/Searle Corporation, Arlington Naights, Illinois. Contents from capsule containing 150 µCi was emptied into 100 ml of deionized-distilled water to give 694.8 ppm of ^{36}Cl.

Solutions used for miscible displacements were prepared to contain 12.5 µCi/liter as ^{36}Cl (57.9 ppm), 12.5 µCi/liter as ^{14}C (0.000326 ppm), and 5 ppm non-labeled 2,4-D dissolved in 0.01 N $CaSO_4$ solution with 0.5% phenol. A 0.01 N $CaSO_4$ solution with 0.5% phenol was used as herbicide and chloride-free irrigation water in all laboratory experiments.

Analyses of the labeled 2,4-D and chloride were performed by liquid scintillation counting with a Packard model 314ETRI-CARB series spectrometer with bi-alkali photomultiplier tubes. Counting efficiencies for ^{14}C and ^{36}Cl were 46% and 93%, respectively, using a dioxane base scintillation cocktail mixture (Aquasol Universal LSC cocktail, New England Nuclear). A 0.10 ml of soil solution was added to 5.0 ml of LSC cocktail for counting the ^{14}C and ^{36}Cl throughout this study. The lower energy channel was used to count ^{14}C with spectrometer settings of 50 for the lower discriminator, and 220 for the upper one, with 7% gain. The upper energy channel was used to count ^{36}Cl with settings of 300 and 1000 for the lower and upper discriminators, respectively, with 2% gain. The photomultiplier tubes were supplied with a high voltage setting of 980 volts.

Concentrations of 2,4-D herbicide were determined by radio assay of ^{14}C on the carboxyl radical but the concentration of Cl ion was determined by the radio essay of ^{36}Cl atom.

Solute Adsorption Isotherm and Kinetics

Adsorption of 2,4-D herbicide on Lakeland fine sand soil material with and without organic matter was studied for non-equilibrium and equilibrium states. Duplicate 5 grams of soil material (oven-dry) were weighed into 15 ml capacity glass tubes of 1.7 cm diameter and 13 cm length. Stock solutions of radioactive 2,4-D were prepared from the main stock solution described previously to give 10, 8, 6, 4, and 2 ppm concentrations in 0.01 N $CaSO_4$ with 0.5% phenol. From each concentration (including zero), 5 ml of solution was added to each tube. To determine the kinetics of the 2,4-D adsorption reaction (the non-equilibrium state) the soil and 2,4-D solution were shaken for 0, 5, 10, 15, 30, 60, 120, 240, 480, 960, and 1440 minutes using all previously mentioned concentrations of ^{14}C-labeled 2,4-D. To obtain the equilibrium adsorption isotherm, soil and the 2,4-D solution were allowed to come to equilibrium by shaking them for 8 hours. Shaking was done in a constant temperature chamber at 25 ± 1°C (Gilson Medical Electronics, Inc., Middleton, Wisconsin). All samples were centrifuged at 3000 rpm for 5 minutes in a IEC centrifuge (Model HN-S, Damon/IEC Division, Needham Heights, Massachusetts). One-half ml of supernatent liquid was pipetted into scintillation vials containing 5 ml of Aquasol Universal LSC and counted in the liquid scintillation spectrometer. Similar counting was done on the stock solutions. The concentration of 2,4-D adsorbed onto the soil (µg/g soil) was plotted against the time of shaking or the solution concentration (µg/cm^3).

Solute Dispersion Coefficients Measurement

Using the miscible displacement technique, the relationship between dispersion coefficients of 2,4-D or chloride and pore-water velocities under both water-saturated and unsaturated conditions were determined in the laboratory. The undisturbed Lakeland fine sand (45.5 cm^2 x 7.6 cm) cores were saturated with solute-free water (0.01 N $CaSO_4$ with 0.5% phenol) and placed in pressure chambers. The physical set-up of the flow system is described in detail by Kanchanasut*(1974). The calculations of dispersion coefficient values were employed by 4 approaches; those of Kirkham and Power (1972), Brenner (1962), Nashimato et al. (1964), and Rose and Passioura (1971). Corrections were made calculating (V/V_o) the pore volumes ratio, to account for the pore volume of the top porous plate, bottom plate and reservoir, since these corrections were not made by Kanchanasut*(1974).

Degradation of 2,4-D in the Columns

The C atom on the carboxyl group of the 2,4-D molecule was radioactively labeled in the solute used. Thin layer chromatographic analyses for 2,4-D in some soil solution samples were therefore made to detect possible microbial and/or chemical breakdown of 2,4-D in the soil columns during displacement. Here a streak of radioactivity distribution on the chromatogram or zones (blobs) should indicate degradation products. A few soil solution samples were selected at random for these analyses. About 1/2 ml of aqueous sample was placed in a 5 ml centrifuge tube. The pH was adjusted to about 3 and then 2,4-D was extracted by ethyl ether. The extracted sample volume was reduced to approximately 15 to 20 microliters

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* Kanchanasut, P. 1974. Influence of soil water content and flow velocity upon miscible displacement of phosphate and chloride in the undisturbed cores of spodosols. Unpublished M.S. thesis, University of Florida, Gainesville, Florida, 32611.

under a steady stream of nitrogen gas. The concentrated sample was drawn into a fine capillary tube by dipping the capillary tube into the liquid. All the liquid in the capillary tube was spotted on a TLC (thin layer chromatographic) plate. Spotting was done at an interval of 1 cm between the spots on a straight line 3.0 cm from the bottom of the TLC plate. All precautions were taken to see that the spots were as small as possible by depositing very little solution on the spot at a time and allowing it to dry before depositing the remainder from the capillary tube. The TLC plates were precoated silica gel type G on glass sheet of size 20 x 18 cm with coating thickness of 250 μ. The TLC plate thus spotted was dried and placed in a glass trough containing the developing solvent. The solvent used for development of a chromatogram of 2,4-D was a mixture of isopropyl alchohol, ammonium hydroxide and water at a ratio of 8:1:1 by volume, respectively. The plate was removed from the bath when the wetting front of the solution reached 10 cm height from the original spots and then dried by evaporation under a hood. Radioactivity distribution on the chromatogram was determined by autoradiograph on x-ray film. The dried plate was placed in contact with Kodak no-screen x-ray film and allowed an exposure of 72 hours in the darkroom. The x-ray film was later developed with x-ray film developer and fixer.

A gas chromatographic method of Meagher (1966) as modified by Wheeler (personal communication) was used to determined 2,4-D concentration in some soil solution samples which were used in TLC analyses.

RESULTS AND DISCUSSION

Soil Analyses

Selected physical properties of the surface soil of Lakeland fine sand are presented in Table 1. The soil material had a low organic matter content, low cation exchange capacity, and low silt and clay contents. Particle size distribution in Table 2 showed a predominance of sand (more than 98%) fraction concentrated within the size range of 0.5 to 0.105 mm. The large value of water-saturated hydraulic conductivity (14.8 cm/hr) coupled with low organic matter, silt and clay content provide a high potential for water and solute movement through Lakeland fine sand. Pore size distribution of undisturbed soil cores was calculated from the equilibrium soil water content-pressure head characteristic curve (Elzeftawy and Mansell, 1975) presented in Table 3. More than 80% of the soil pores occurred within the range of 1000 to 25 micron of effective diameter. Note that the 25μ effective diameter soil pores would retain water up to 118.66 cm of water suction.

The soil water content-suction characteristic curve determined during infiltration of water is shown in Figure 1. The steep slope of $\theta(h)$ curve (large $\frac{\partial\theta}{\partial h}$) is typical of sands. Notice that the degree of water saturation was less than 24% (θ approximately 9% in comparison to θ_{sat} of 37.4%) for a soil water suction of 100 cm of water.

The calculated and measured hydraulic conductivities of Lakeland fine sand are shown in Figure 2. The solid line is calculated from the static equilibrium soil water content-suction characteristic curve using the saturated hydraulic conductivity value as a matching factor as described by Elzaftawy and Mansell (1975). The measured hydraulic conductivity values were calculated by essentially the same technique used

Table 1. Selected physical properties of Lakeland fine sand.

% sand	98.38
% silt	1.61
% clay	0.74
% organic matter	0.51
CEC meq/100g	0.83
bulk density*, g/cm^3	1.56
% water **	0.65
saturated hydraulic conductivity, cm/hr	14.80
porosity	0.37
^{137}Cs mass adsorption coefficient, μ_s, cm^2/g	0.0772
^{241}Am mass adsorption coefficient, μ_s, cm^2/g	0.2560

* From the undisturbed cores (average of 3 samples).
** At the time of packing, on oven dry weight basis.

Table 2. Particle size distribution of Lakeland fine sand

Size Range mm	Particle size distribution %
2 - 1	0.45
1 - 0.5	4.34
0.5 - 0.25	65.38
0.25 - 0.105	21.59
0.105 - 0.053	6.62
0.053 - 0.002	1.61
less than 0.002	0.74

Table 3. Pore size distribution of Lakeland fine sand.

Effective diameter μ	Suction Range cm	Pore size distribution * %
> 1000	0 - 2.97	1.50
1000 - 750	2.97 - 3.96	1.34
750 - 500	3.96 - 5.93	0.53
500 - 250	5.93 - 11.87	1.60
250 - 100	11.87 - 29.66	38.78
100 - 75	29.66 - 39.55	13.37
75 - 50	39.55 - 59.33	14.71
50 - 25	59.33 - 118.66	10.70
<25	>118.66	17.47

* Calculated from soil water content-pressure characteristic curve using the law h = 4σ/2rρg where 2r=diameter of pores, σ=72.75 dynes/cm at 20°C, g=981 dynes/g, and ρ=1.00 g/cm^3.

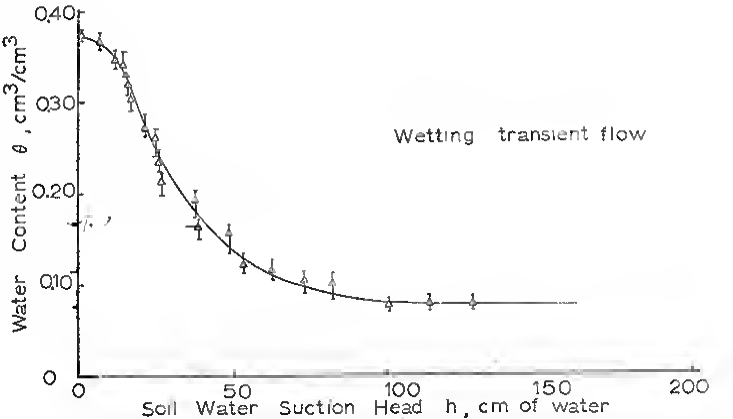

Figure 1. Soil water content-suction characteristic curve of Lakeland fine sand

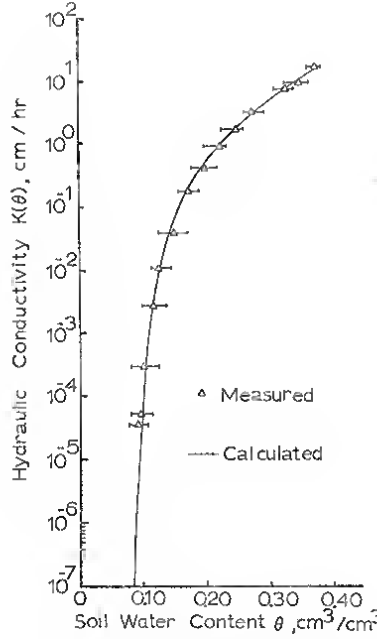

Figure 2. Calculated and measured hydraulic conductivities of Lakeland fine sand.

by Vachaud (1967). The Darcy flux V and the hydraulic gradient ∇H were determined from the water content and hydraulic head profiles and conductivity was calculated from Darcy's law, i.e. from the ratio of flux to hydraulic gradient. The triangle points and the horizontal solid lines represent the average values and the range of the hydraulic conductivities determined during all the soil column experiments. Agreement between measured and calculated unsaturated hydraulic conductivities is excellent for water saturations greater than 27% (volumetric water contents between 10 and 37 percent). The deviation between calculated and measured values is pronounced for volumetric water content less than 10 percent. The measured unsaturated hydraulic conductivities have higher values than the calculated ones for water saturation less than 27%.

The curve in Figure 2 was expressed with the following hydraulic conductivity-water content relationships in the FORTRAN IV computer program developed by Selim et al. (1974).

$$K(\theta) = \exp[5.512272 \ln \theta + 8.115944] \quad \theta \geq 0.19 \qquad [34]$$

$$K(\theta) = \exp[7.932661 \ln \theta + 12.135590] \quad 0.14 \leq \theta < 0.19 \qquad [35]$$

$$K(\theta) = \exp[11.749519 \ln \theta + 19.639932] \quad \theta < 0.14 \qquad [36]$$

Using equation [11], the soil water diffusivity-water content relationships were calculated and utilized in the same computer program as follows:

$$D(\theta) = \exp[25.775475\,\theta - 0.124657] \quad \theta \geq 0.20 \qquad [37]$$

$$D(\theta) = \exp[18.698562\,\theta + 1.292726] \quad 0.15 \leq \theta < 0.20 \qquad [38]$$

$$D(\theta) = \exp[37.519046\,\theta - 1.531967] \quad 0.12 \leq \theta < 0.15 \qquad [39]$$

$$D(\theta) = \exp[104.03433\,\theta - 9.513706] \quad 0.11 \leq \theta < 0.12 \qquad [40]$$

$$D(\theta) = \exp[30.282606\,\theta - 1.401056] \quad \theta < 0.11 \qquad [41]$$

Degradation of 2,4-D in the Columns

An attempt was made to evaluate if 2,4-D herbicide underwent degradation in the soil columns when the solute and displacing water (solute-free water) contained 0.5% phenol. The results of thin layer chromatographic analyses on the soil solution samples are presented in Figure 3. In the figure, the numbers 1, 3, 5, and 7 correspond to stock solution, 2 and 4 to soil solution extracted from the soil columns, 6 to soil extraction of incubated soil sample with stock solution at 25°C for 35 hours. Radioactivity in the chromatogram for the standard solutions, the soil effluents from soil columns, and soil extraction of the incubated sample moved with 2,4-D molecules approximately equal distances from the starting point. The R_f value (ratio of distance traveled by the zone of concentration to that by wetting front) is found to be, on the average, 0.78. If degradation of the herbicide had occurred in the soil columns, radioactivity would have distributed along the chromatogram in the form of a streak or a string of small globules each globule representing one degraded product.

To make sure that there was no herbicide degradation in soil, the same soil solution of samples number 2, 4, and 6 were used to determine the 2,4-D concentration utilizing the gas chromatographic method. The results showed that 98% recovery was obtained for the samples used. Thus, we may conclude that 2,4-D did not disintegrate during the relatively short periods (10 hours) for movement through columns of Lakeland fine sand. Hamaker (1972) reported that the average time for 50% disappearance of applied 2,4-D herbicide in soil is 17 days for conditions of laboratory incubation at 26°C.

Figure 3. Results of thin layer chromatograph analyses of 2,4-D on selected soil solution samples.

Rate of 2,4-D Adsorption

The rates of 2,4-D adsorption in Lakeland fine sand for concentrations of 2, 6, 8, and 10 are presented in Figure 4. For all concentrations, the rate was very high during the early adsorption process and it decreases with time. It can be concluded that the rate of 2,4-D adsorption is practically equal to zero after 2 hours for all initial solute concentration used. Figure 5 shows the rate of 2,4-D adsorption in Lakeland fine sand using solute concentration of 6 ppm. The herbicide was adsorbed rapidly during the first hour and slowly afterward. The rates of adsorption, $\frac{\partial S}{\partial t}$, calculated from the data best fit curve were 0.013, 0.007, and 0.002 at 5, 10, and 30 minutes, respectively for 6 ppm concentration.

2,4-D Adsorption and Desorption Isotherms

Figure 6 shows the relation between S, quantity of herbicide adsorbed per gram of soil (μg/g), and C, the equilibrium herbicide concentration in solution (μg/ml), for 2,4-D at equilibrium with Lakeland fine sand with and without organic matter. Generally speaking, 2,4-D adsorption followed the Freundlich adsorption equation in the form:

$$S = K C^{1/n} \qquad [42]$$

where K, the distribution coefficient, is equal to the 0.134 (ml/g) for the soil with organic matter and 0.046 for the soil without organic matter. Using equation [42] to describe 2,4-D adsorption by Lakeland soil, the value 1/n is nearly one and it can be assumed unity. Only ½% of organic matter resulted in a K value almost 3 times as large as for the soil with the organic matter removed. Thus O.M. has an important contribution to adsorption-desorption of 2,4-D in Lakeland sand.

Equilibrium desorption isotherms for 2,4-D were obtained using a

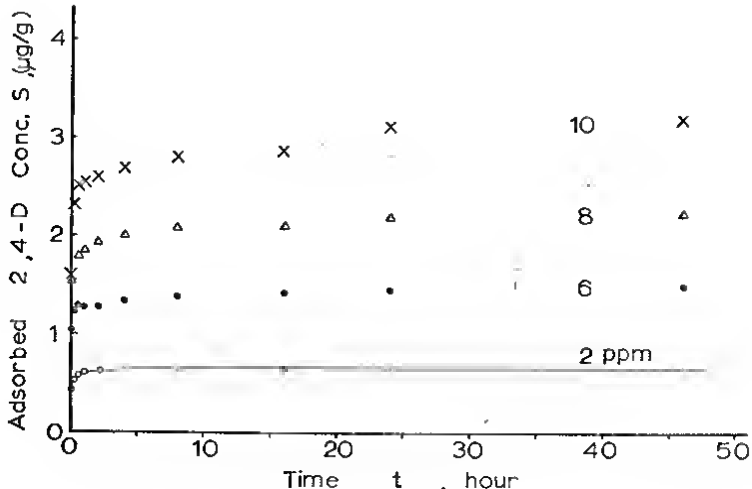

Figure 4 Rate of 2,4-D adsorption on Lakeland sand for selected concentrations.

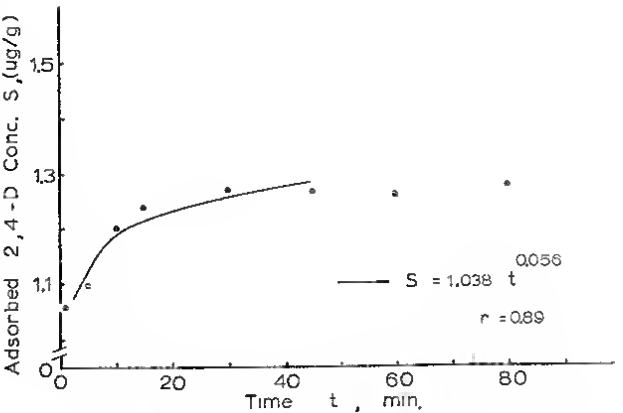

Figure 5 Rate of 2,4-D adsorption on Lakeland fine sand for 6 ppm concentration.

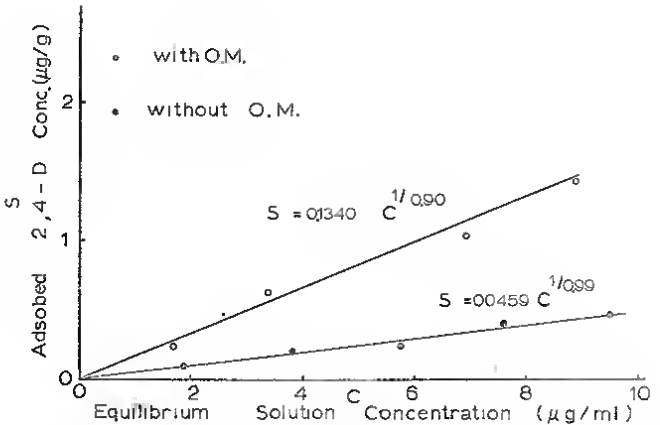

Figure 6. Equilibrium adsorption isotherms of 2,4-D on Lakeland fine sand with and without organic matter.

laboratory procedure similar to Davidson and McDougal (1973). As can be seen from Figure 7, adsorption and desorption of 2,4-D were not described by a single-valued function. For adsorption, the value of the adsorption distribution coefficient, k_a, and constant 1/n, were 0.134 (ml/g) and 1.103, respectively. The desorption distribution coefficient, k_d, were more than two times larger than those obtained for adsorption and vary with the maximum concentration absorbed. The desorption data is described by equation (42), but the parameters k_d and 1/n vary with the adsorbed concentration of 2,4-D existing prior to the initiation of desorption. Thus data shown in Figure 7 indicate that the adsorption-desorption reaction of 2,4-D in Lakeland soil favors adsorption over desorption. This nonsingularity should result in development of residues of 2,4-D in this soil.

Soil Water Measurement

The mass absorption coefficients for 60 and 662 keV gamma radiation of Lakeland soil and water were determined from attenuation measurements. The 60 and 662 keV attenuation coefficients for water when the photon beam was monoenergetic, 0.2010 $\pm$ 0.0007 and 0.0832 $\pm$ 0.0005 cm^2/g, respectively, were in good agreement with the theoretical (Gradstein, 1957) values of 0.2040 and 0.0857 cm^2/g. When both Cs and Am capsules were in place, the 60 and 662 keV coefficients for water, 0.1984 and 0.0841 cm^2/g, were also in good agreement with these theoretical values. These coefficients were used to evaluate soil water contents and bulk densities of the soil columns.

For the measurement of rapidly changing soil water pressure, Watson (1965) reported that it is necessary to have a response time, τ, as small as possible, recognizing that the selection of the air entry value

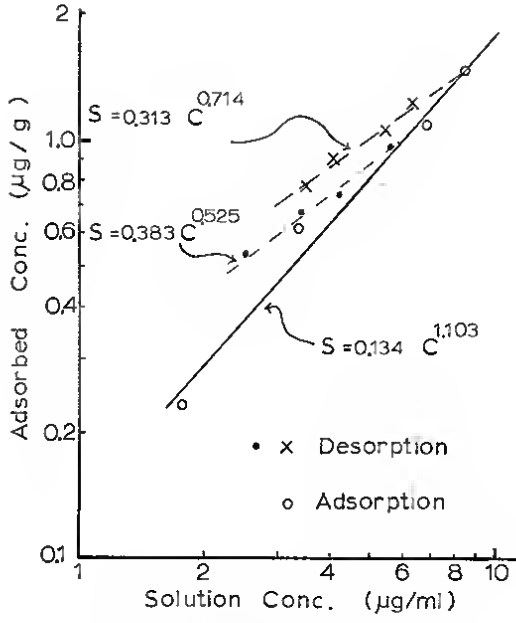

Figure 7. Adsorption-desorption equilibrium isotherms of 2,4-D on Lakeland fine sand.

of the porous tensiometer used will influence τ. The pressure transducer used here has excellent volume displacement-pressure characteristic and accordingly facilitates a system having a small response time. Table 4 shows the soil-tensiometer cup water conductance, k, for water and saturated and unsaturated soil. The response time-constant of the tensiometer-transducer system when the tensiometer cup was immersed in water or in water-saturated soil was 0.1 sec. But the response became quite large ($\geq$ 15 seconds) when the soil was water-unsaturated. Rapid decrease of hydraulic conductivity of the soil with decreasing water content caused an increase in the time required for the transmission of water through the porous medium to or from the tensiometer cup. When the porous cup is placed in water τ is limited by the cup conductance, however, when the cup is in soil the soil hydraulic conductivity limits the response time-constant, τ, (Richards, 1949). Klute and Gardner (1962) looked at the tensiometer response from the viewpoint of instrument or soil limiting factors. They presented the theory of tensiometer response and its exact solution where the instrument is the limiting factor. However, the solution of the tensiometer response problem when the soil is limiting are not yet available (Watson, 1966).

Dispersion Coefficient Analyses

The dispersion coefficient values of ^{36}Cl and 2,4-D for a pore-water velocity of 7.92 cm/hr (flux = 1.98 cm/hr and θ = 0.25 cm^3/cm^3) were calculated from breakthrough curves using the miscible displacement technique and are reported in Table 5. The calculations employed 4 approaches, those of Kirkham and Power (1972), Brenner (1962), Hashimoto et al. (1964), and Rose and Passioura (1971). It should be noted that the Rose and Passioura method has a practical advantage over the others,

Table 4. Soil-tensiometer cup water conductance under saturated and unsaturated conditions

	Response time-constant, τ sec.	Conductance, k* $cm^3/hr/cm$ of water
In water	0.1	5.08×10^{-1} **
saturated soil	0.1	5.08×10^{-1}
unsaturated soil	0.3	1.69×10^{-1}
	10.0	5.08×10^{-3}
	15.0	3.24×10^{-5}

* Calculated using equation [33].
** Cup conductance as defined by Richards (1949)

Table 5. Dispersion coefficient values of ^{36}Cl and 2,4-D at v=7.92 cm/hr, calculated by 4 different approaches.

Solute	D_s^*			
	Brenner	Hashimato et al.	Kirkham & Power	Rose & Passioura
^{36}Cl	11.0	10.9	10.2	12.0
2,4-D	3.0	3.1	2.9	3.1

* D_s in cm^2/hr.

since it gives nearly perfect straight lines over a wide range of pore-water velocities and thus shows clearly small deviations from ideal behaviour.

Figure 8 shows the relationships between dispersion coefficient and average pore-water velocity of ^{36}Cl and 2,4-D under saturated and unsaturated steady-state flow conditions in Lakeland sand. It should be mentioned that these relationships are only valid within the range of 4.45 to 26.33 (cm/hr) of pore-water velocities. Kirda et al. (1973) reported that the molecular diffusion coefficient for chloride corrected for the conditions of soil is within the range of 2.58×10^{-2} (cm^2/hr) for transient water flow conditions in loamy soil. Although the relation suggested by Harleman and Rumer (1962) is an empirical relation, it has been found to be slightly lower than the apparent diffusion coefficients reported for steady-state conditions (Kirda et al., 1973). Saxena et al. (1974) calculated the dispersion coefficient of 2,4-D from the experimental dispersion profiles in a non-sorbing glass beads porous media. Glass beads with predominant pore radii of 4, 5, 8.2, 13.5, and 36.2 μm had 2,4-D dispersion coefficients of 0.022, 0.029, 0.059, and 0.086 cm^2/hr, respectively. They also reported that the theoretical distributions of the 2,4-D in the columns were found to be in good agreement with the experimental determined distributions. These reported values of dispersion coefficients were determined using mean velocity of 2.08 cm/hr under saturated conditions. In a sandy soil similar to Lakeland fine sand we expect higher values of dispersion coefficients because of the large percentage of big pores (38-78% in range of 250-100μ in Table 3) especially under transient unsaturated water flow. Scott and Phillips (1974) measured the self-diffusion coefficient of 2,4-D in water at 23°C. They reported

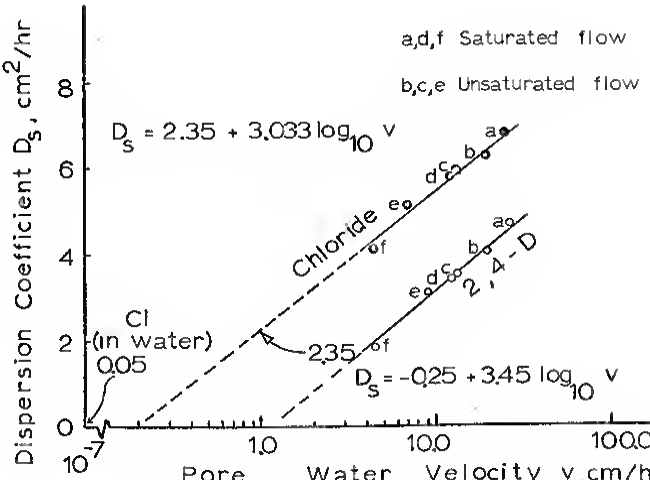

Figure 8, Relationships of chloride and 2,4-D dispersion coefficients and pore water velocity under saturated and unsaturated flow conditions (a, b, c, d, e, and f correspond to water content, θ, 0.37, 0.35, 0.30, 0.37, 0.25, and 0.37, respectively) in Lakeland fine sand.

a value of approximately 2.1×10^{-2} cm^2/hr. This measured diffusion coefficient can be used as the minimum value of 2,4-D dispersion coefficient when the pore-water velocity reaches zero when corrected for the condition of soil (tortuosity and water content).

The relations shown in Figure 8 were used to calculate the chloride and 2,4-D distribution profiles during their simultaneous movement with water in soil columns. It was assumed in the computer program that the minimum value of the chloride dispersion coefficient is equal to 0.04 cm^2/hr when the pore-water velocity is equal to or less than 0.30 cm/hr. Hodgman (1944) reported that the self-diffusion coefficient of KCl is equal to 0.05 cm^2/hr in pure water at 17°C.

Column Packing

The change in the soil bulk density from initial packing to the time of termination of the column experiments can be seen in Figure 9. Determinations of the bulk density were made using the gamma readings before and after each column experiment. The results in Figure 9 shows only those from four of the nine columns. Each point represents the average of two columns. Assuming an overall average bulk density of 1.56 g/cm^3 along the soil column during all experiments is a reasonable approximation. As expected the changes in bulk density during water infiltration in Lakeland sand was negligible due to the fact that this soil had less than 2.5% silt and clay fraction (Table 1) and was mostly comprised of sand particles.

Watson (1966) reported an almost unbelievable uniformity of packing. His technique of packing under water works well with a sand having a narrow pore size range. If one wishes to pack a soil or even a sand with a wide range of particle sizes, Watson's technique has limitations because

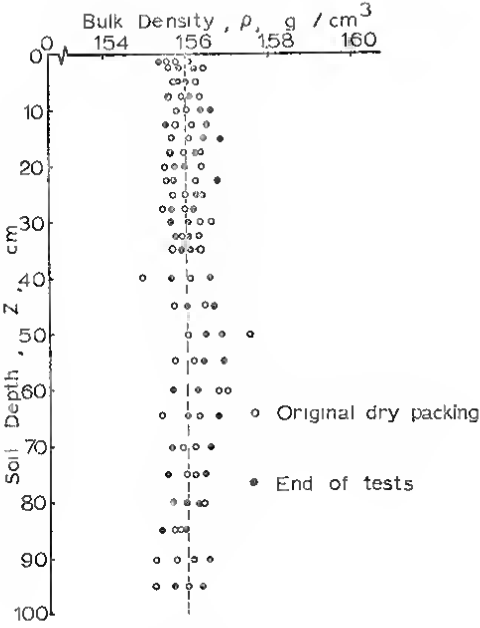

Figure 9 Bulk density along the sand column

of particle size separation by sedimentation, and in the case of soils containing aggregates, slaking of the aggregate. Dry packing is a more realistic technique but it also leads to bulk density variations as found in this study.

Movement of Water, Chloride, and 2,4-D

The simultaneous movement of water and solute through soil will be affected by the initial and boundary conditions of the soil-water system. In this study, influences of the initial soil water content and the water flux at the soil surface upon the simultaneous movement of water, chloride and 2,4-D will be discussed.

The Effect of Surface Water Flux

Sets of Figures 10, 11, and 12; 13, 14, and 15, and 16, 17, and 18 show the effect of application of constant surface water flux of 2, 4, and 8 cm/hr, respectively, upon the movement of water, chloride, and 2,4-D herbicide under different initial water contents, θ_i.

During the early stages of infiltration of water, the surface soil-water content increased with a decreasing rate until a steady value was achieved. This constant value is the soil-water content which corresponds to the hydraulic conductivity that equals the applied surface water flux ($\frac{\partial \theta}{\partial z}$ and $\frac{\partial^2 \theta}{\partial z^2}$ are equal to zero). For water flux of 2 cm/hr, for example, (Figures 10a, 11a, and 12a) the surface soil-water content, θ, reached approximately 0.26 cm^3/cm^3 regardless of the initial soil-water content. Figure 2 shows that the hydraulic conductivity of Lakeland soil is about 2 cm/hr at θ equal to 0.26. It should be mentioned that similar results were observed for water fluxes of 4 and 8 cm/hr. For water fluxes of 4 and 8 cm/hr (Figures 13a, 14a, 15a, 16a, 17a, and 18a) the soil-water content at the surface reached about 0.294 and 0.315 cm^3/cm^3, respectively

The effect of surface water flux upon the movement of the water front can be shown in Figures 11a, 14a, and 17a for initial soil water content of 0.109 cm^3/cm^3. After one hour of water application at the soil surface the advancing water front had reached approximately 21, 30, and 47 cm depth for water fluxes 2, 4, and 8 cm/hr, respectively. Philip (1957) showed that the ultimate velocity of the advancing water front down the soil profile is

$$\left(\frac{\partial z}{\partial t}\right)_{\text{ultimate}} = \frac{K_s(\theta) - K_i(\theta)}{\theta_s - \theta_i} \qquad [43]$$

where K and θ are the hydraulic conductivity and soil-water content, respectively. The subscript (s) denotes soil surface. Since $K(\theta)$ increases with θ at a faster-than-linear rate, it is clear that an increase in θ_i produces a bigger percentage affect on $(\theta_s - \theta_i)$ then on $[K_s(\theta) - K_i(\theta)]$. Hence, an increase of initial water content produces an increase in the rate of advance down the soil column. For water flux of 2 cm/hr, for example, the ultimate velocities of the water front are 8.06, 12.44, and 13.79 cm/hr for initial soil-water contents 0.012, 0.102, and 0.202, respectively. Since the water front was never allowed to reach the proximity of the bottom of the soil column during all experiments, the columns were sufficiently long to be considered semi-infinite media. Solving the nonlinear partial differential equation of water by Selim et al., (1974) numerically and utilizing their computer program, Figures 11a, 14a, and 17a show the calculated and experimental soil-water distributions for corresponding water fluxes of 2, 4, 8 cm/hr. We can conclude from these results that calculated and experimental data were in excellent agreement.

Applying water with different flux at the soil surface affected movement of surface-applied chloride through the soil. Figures 11b, 14b,

and 17b shows experimental and calculated results of chloride (^{36}Cl) distributions in soil solution of Lakeland fine sand for water fluxes 2, 4, and 8 cm/hr, respectively. The initial soil water content was 0.109 cm^3/cm^3 before applying 2 cm of solute which contained ^{36}Cl and 2,4-D. Using the relation between the apparent diffusion coefficient and pore water velocity (Figure 8), the calculated chloride distributions were in good agreement with the experimental results for all experiments (Figures 11b, 14b, and 17b). The depths of maximum concentrations of chloride after one hour of water application were 4, 7.5, and 14 cm for water fluxes, 2, 4, and 8 cm/hr, respectively, that is to say the high rate of water application caused the chloride to move deeper into the soil. However, during infiltration a given quantity of water gave rise to a deeper displacement of chloride for lower values of the surface water flux. This behavior is illustrated in Figures 11b, 14b, and 17b, by comparing the depth of the maximum chloride concentration following 8 cm of water application. Kirda et al. (1973) obtained similar results of chloride movement under controlled surface water content but with constant head boundary conditions in laboratory soil column experiments.

The 2,4-D concentration with depth at various times for surface water fluxes of 2, 4, and 8 cm/hr are shown in Figures 11c, 14c, and 17c, respectively, with initial soil water content of 0.109 cm^3/cm^3. The decreases in peak height and the increased spreading with time are a result of mixing by diffusion and velocity dispersion of 2,4-D during flow through soil pores. The tailing (Figure 11c) which is particularly pronounced at longer times of water infiltration indicates the presence of a nonsingular relationship between adsorption and desorption of 2,4-D on Lakeland soil. Assuming the instantaneous equilibrium adsorption of

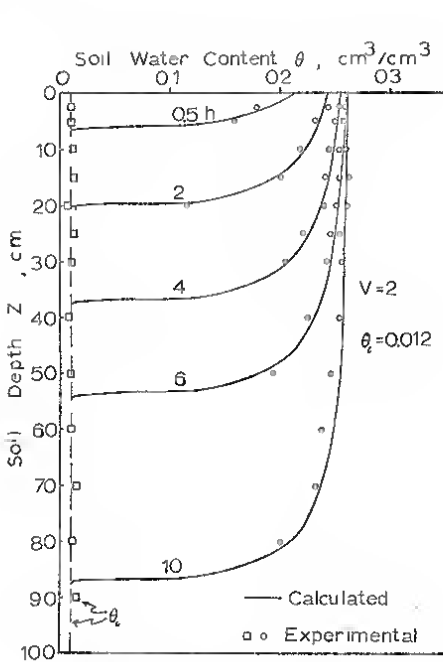

Figure 10a. Calculated and experimental soil water content distributions for 2 cm/hr surface water flux and 0.012 cm^3/cm^3 initial soil water content

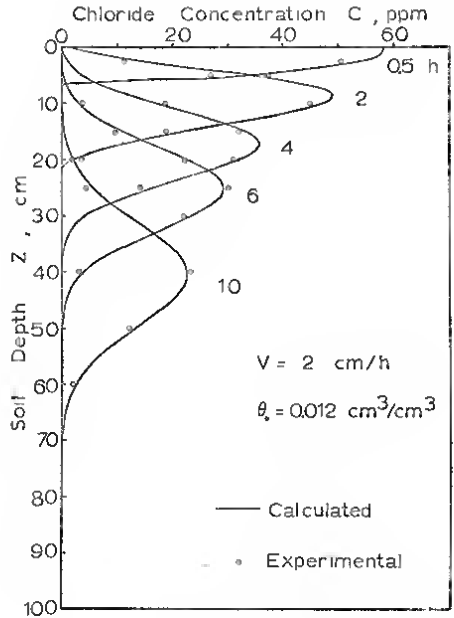

Figure 10b Calculated and experimental chloride distributions for 2 cm/hr surface water flux and 0.012 cm^3/cm^3 initial soil water content.

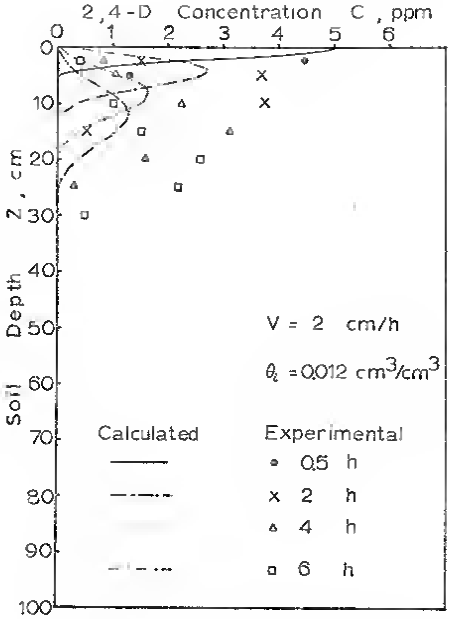

Figure 10c: Calculated and experimental 2,4-D soil solution content distribution for 2 cm/hr surface water flux and 0.012 cm^3/cm^3 initial soil water content.

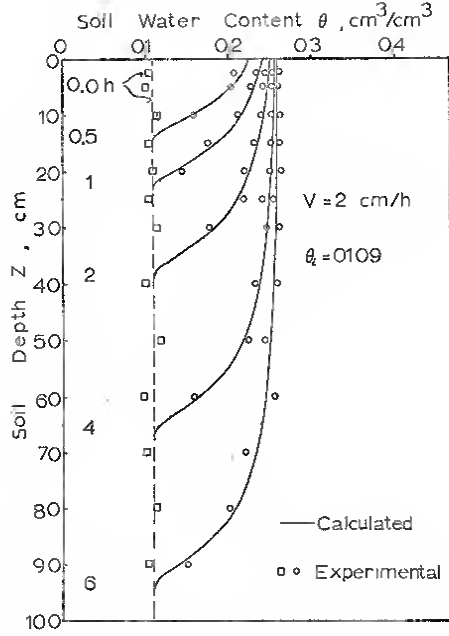

Figure 11- Calculated and experimentel soil water content distributions for 2 cm/hr surfece water flux and 0·109 cm^3/cm^3 initiel soil water content-

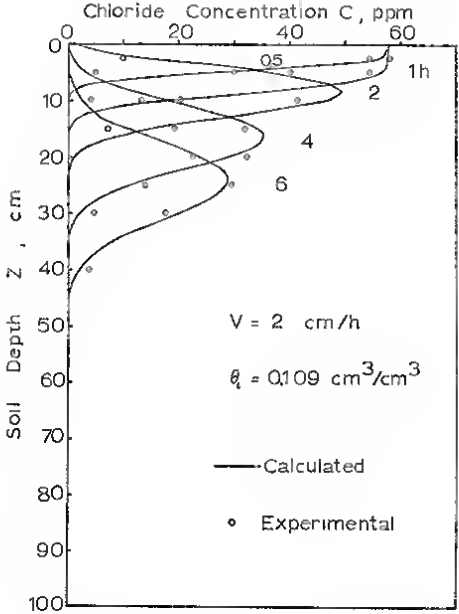

Figure 11b. Calculated and experimental chloride distributions for 2 cm/hr surface water flux and 0.109 cm^3/cm^3 initial soil water content.

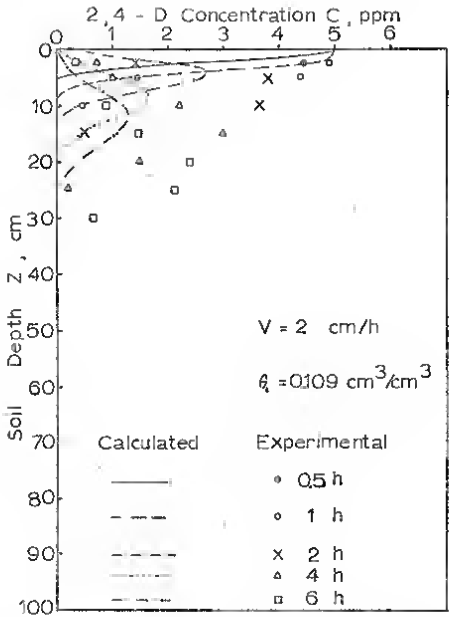

Figure 11c. Calculated and experimental 2,4-D soil solution content distributions for 2 cm/hr surface water flux and 0.109 cm^3/cm^3 initial soil water content.

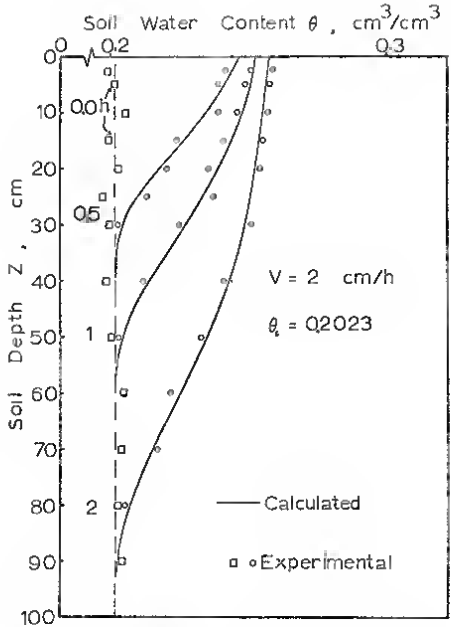

Figure 12a- Calculated and experimental soil water content distributions for 2 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water content.

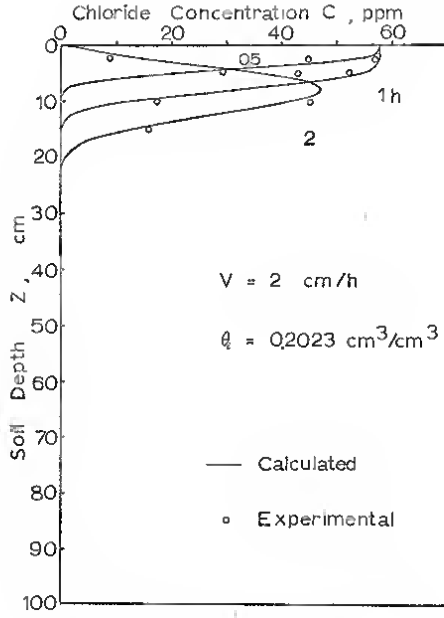

Figure 12b. Calculated and experimental chloride distributions for 2 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water content.

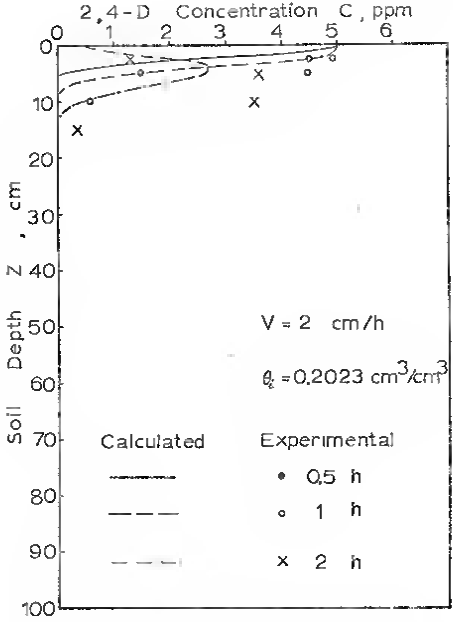

Figure 12c Calculated and experimental 2,4-D soil solution content distributions for 2 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water content.

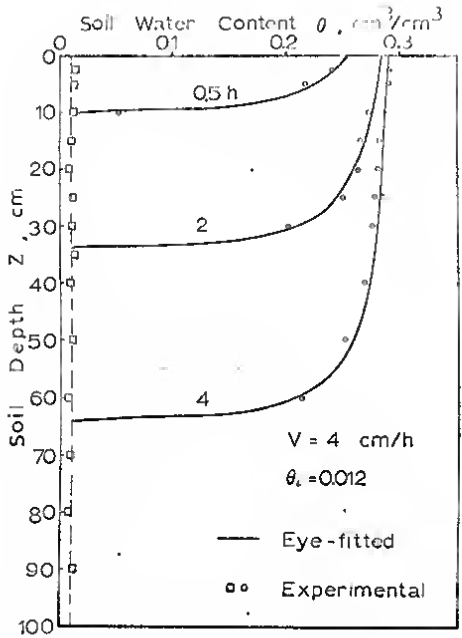

Figure 13a. Experimental soil water content distributions for 4 cm/hr surface water flux and 0.012 cm^3/cm^3 initial soil water content

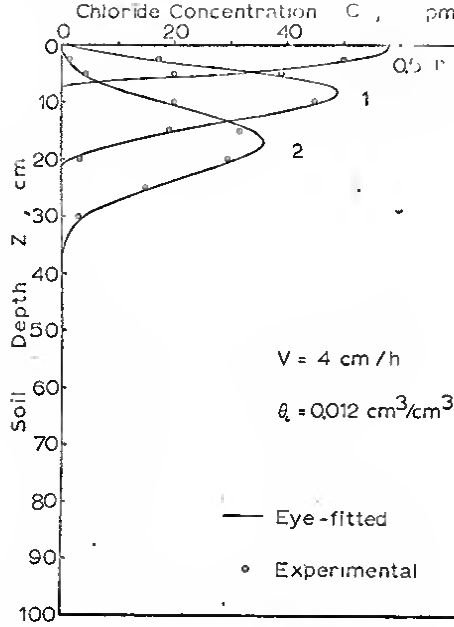

Figure 13b Experimental chloride distributions for 4 cm/hr surface water flux and 0.012 cm^3/cm^3 initial soil water content

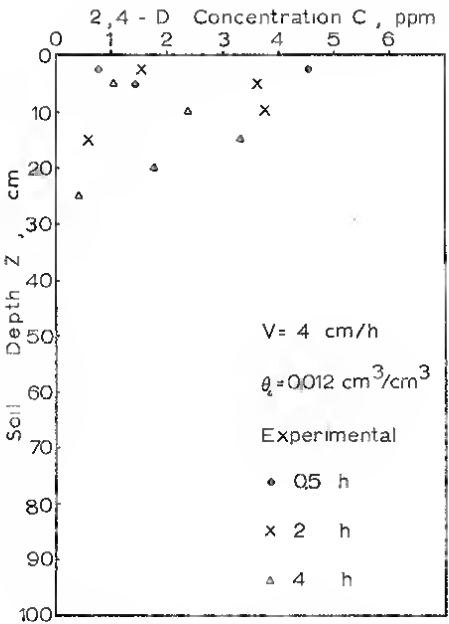

Figure 13c. Experimental 2,4-D soil solution content distributions for 4 cm/hr surface water flux and 0.012 cm^3/cm^3 initial soil water content

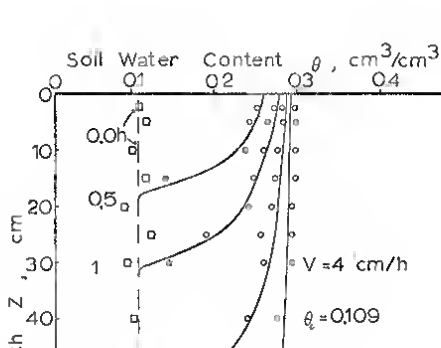

Figure 14a- Calculated and experimental soil water content distributions for 4 cm/hr surface water flux and 0.109 cm^3/cm^3 initial soil water content

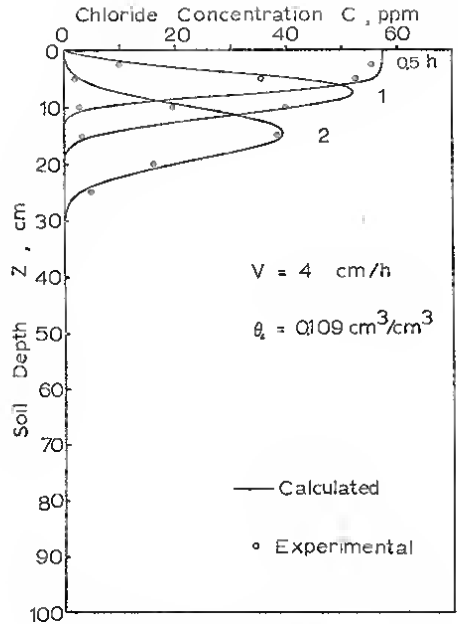

Figure 14b- Calculated and experimental chloride distributions for 4 cm/hr surface water flux and 0.109 cm^3/cm^3 initial soil water content.

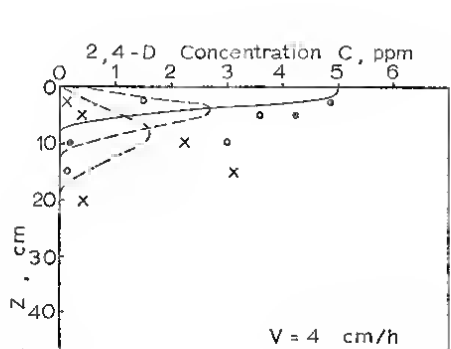

Figure 14c. Calculated and experimental 2,4-D soil solution content distributions for 4 cm/hr surface water flux and 0.109 cm^3/cm^3 initial soil water content.

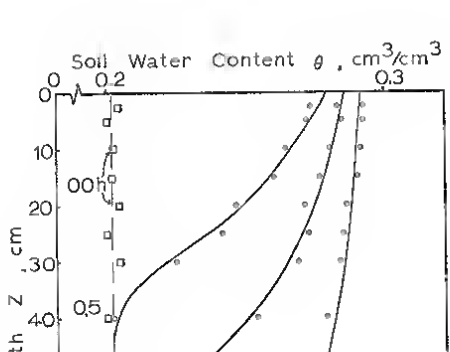

Figure 15a- Calculated and experimental soil water content distributions for 4 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water content

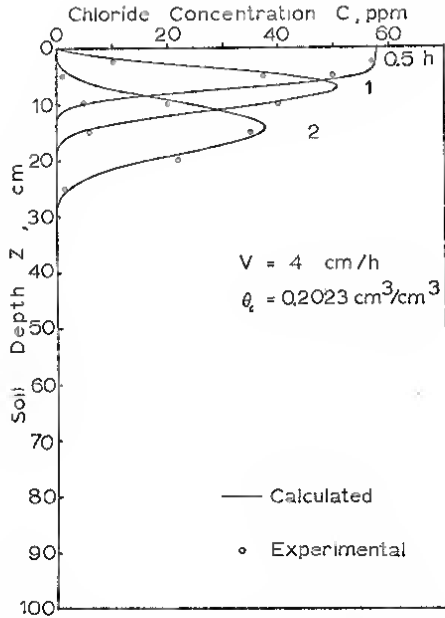

Figure 15b. Calculated and experimental chloride distributions for a 4 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water content.

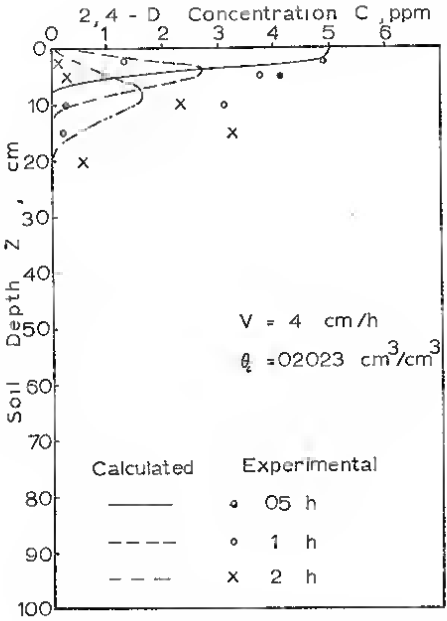

Figure 15c: Calculated and experimental 2,4-D soil solution content distributions for 4 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water content.

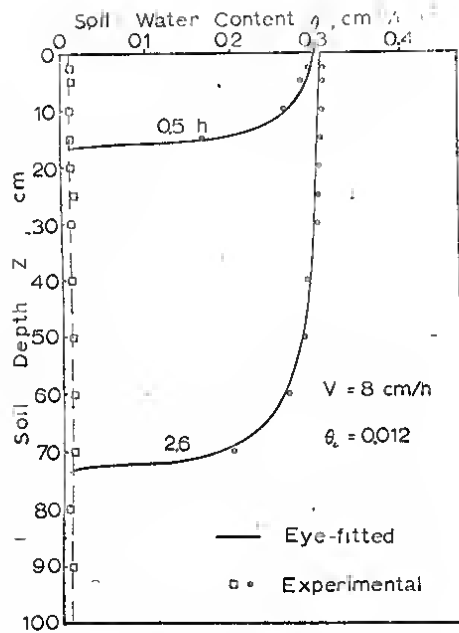

Figure 16a. Experimental soil water content distributions for 8 cm/hr surface flux and 0.012 cm^3/cm^3 initial soil water content

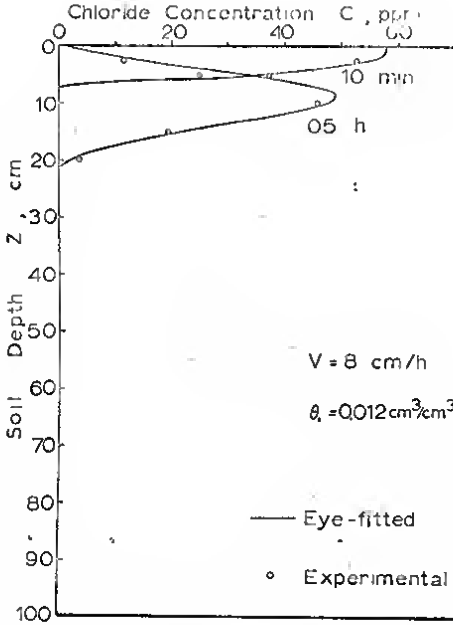

Figure 16b. Experimental chloride distributions for 8 cm/hr surface water flux and 0.012 cm^3/cm^3 initial soil water content.

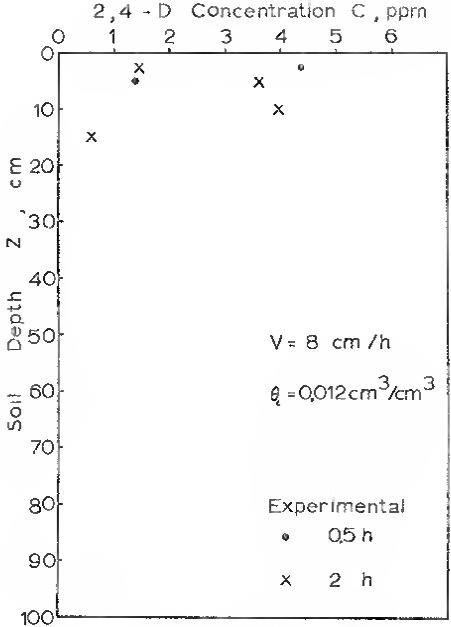

Figure 16c: Experimental 2,4-D soil solution content distributions for 8 cm/hr surface water flux and 0.012 cm^3/cm^3 initial soil water content

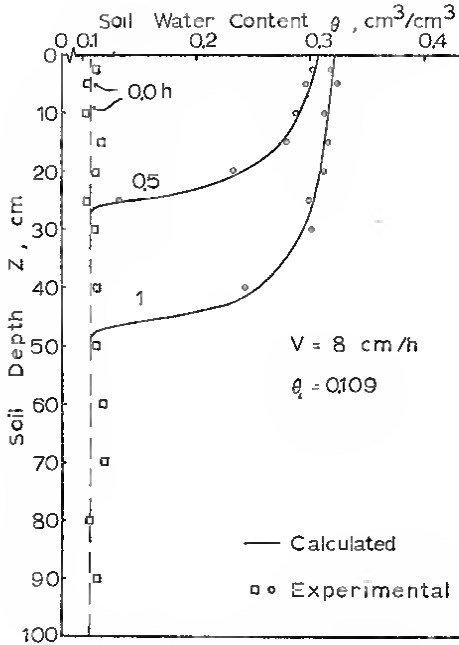

Figure 17e- Calculated and experimental soil water content distributions for 8 cm/hr surface water flux and 0.109 cm^3/cm^3 initial soil water content.

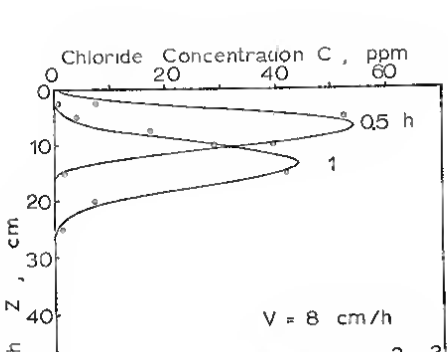

Figure 17b: Calculated and experimental chloride distributions for 8 cm/hr surface water flux and 0.109 cm^3/cm^3 initial soil water content.

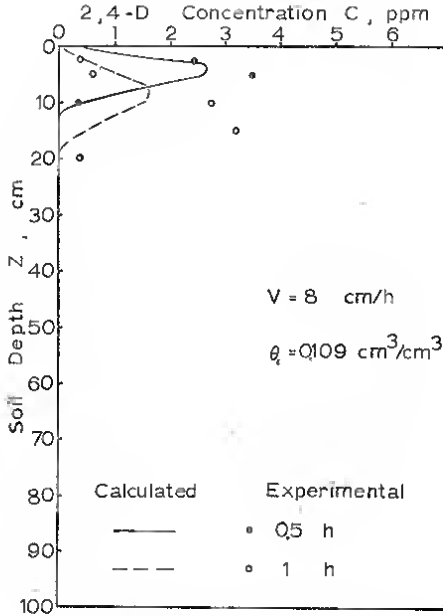

Figure 17c. Calculated and experimental 2,4-D soil solution content distributions for 8 cm/hr surface water flux and 0.109 cm^3/cm^3 initial soil water content.

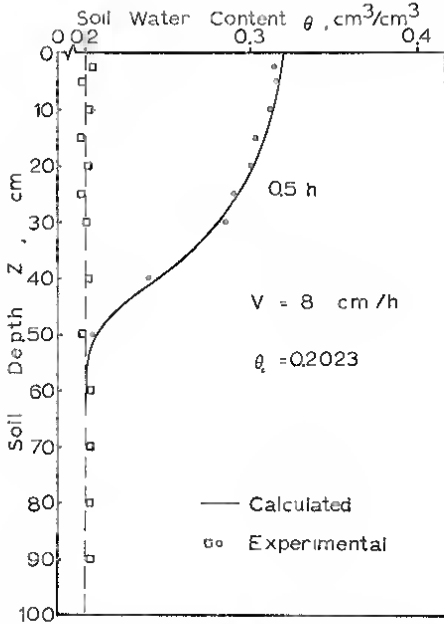

Figure 18a Calculated and experimental soil water content distributions for 8 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water content.

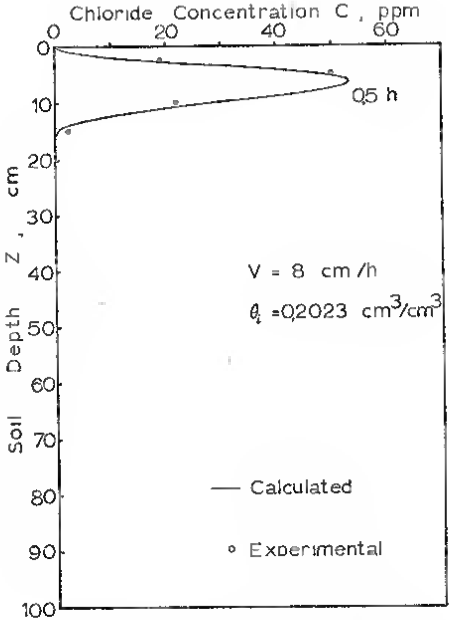

Figura 18b. Calculated and experimental chloride distributions for 8 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water content.

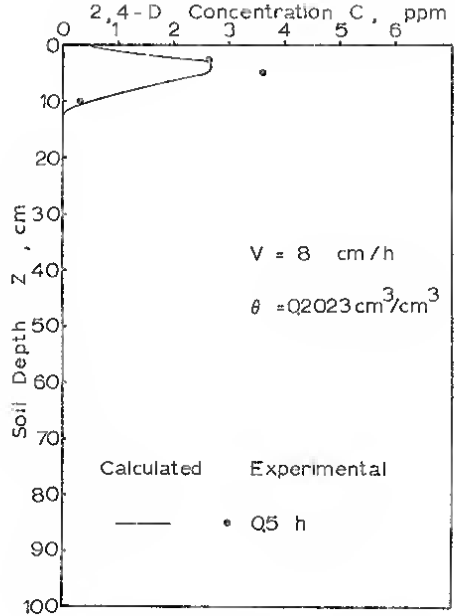

Figure 18c Calculated and experimental 2,4-D soil solution content distributions for 8 cm/hr surface water flux and 0.202 cm^3/cm^3 initial soil water.

2,4-D herbicide by Lakeland soil, the calculated 2,4-D distributions during infiltration were obtained using the following equations, as described by Selim et al. (1974)

$$\frac{\partial S}{\partial t} = \rho K(C) \frac{\partial C}{\partial t} \qquad [44]$$

and

$$R(C) = 1 + \frac{\rho K(C)}{\theta} \qquad [45]$$

where K(C) is the distribution coefficient and R(C) is the retardation factor. The utilized units and definitions of terms are previously mentioned. The comparison between the calculated and experimental results of 2,4-D movement through Lakeland soil can be seen in Figures 10c, 11c, 12c, 14c, 15c, and 17c. The calculated results did not adequately describe the experimentally distributions of 2,4-D herbicide. Using the retardation factor of equation [45] resulted in high values of 2,4-D adsorption by soil. A comparison between Figures 11b and 11c, in which the same initial and boundary conditions of water movement occurred, reveals that the peak of 2,4-D lagged behind the peaks for chloride concentration for all sampling times shown. For example, after six hours of infiltration the peak of 2,4-D resided at soil depth approximately 22 cm in contrast of 25 cm for the chloride.

In general, increasing the soil-surface water content by increasing the water application rate resulted in shallower displacement of chloride and 2,4-D for the same accumulative infiltration under air dry or partially wet Lakeland fine sand soil.

The Effect of Initial Soil-Water Content

Initial value of soil water is well known to influence water intake. During constant irrigation intensity for infiltration into semi-infinite homogeneous profile, the inflow rate approaches a constant rate equal to

the hydraulic conductivity at the surface soil-water content and is independent of the initial soil-water content (Warrick et al., 1971). The time required to attain a constant infiltration rate (constant surface soil-water content) is less for a drier profile and the rates for drier profiles are initially larger than wet profiles. These observations were consistent with the curves shown in Figures 10a, 11a, and 12a. After 1/2 hour of applied surface flux of 2 cm/hr, the surface soil-water content has reached 0.210, 0.228, and 0.248 cm^3/cm^3 for initial soil water contents of 0.012, 0.109, and 0.202 cm^3/cm^3, respectively. These results confirm that the time required to reach a constant soil-water content at the soil surface is less for higher values of initial soil water content. The wetting front penetrated deeper in soil columns with higher initial water content (Figures 10a, 11a, and 12a) after a specific time of water application. Even though the driest profile initially took water at the greatest infiltration rate, the wetting front advanced the least (20 cm, as compared to 38 and 90 cm for initial soil water content 0.012, 0.109, and 0.202 cm^3/cm^3, respectively, after 2 hours of water application). In each case, the rate of water front advance varies with the amount of pore space to be filled between the initial and final values of the soil-water content. Thus the rate of advance of wetting front approaches $V/(\theta_{wet} - \theta_i)$ and is 8.06, 13.25, and 34.48 cm/hr for θ_i of 0.012, 0.109, and 0.202 cm^3/cm^3, respectively, at water flux V=2 cm/hr.

Contrary to the advance of the wetting front, the chloride distributions move nearly independently of initial soil-water content as shown in Figures 10b, 11b, and 12b (where the initial chloride concentration is zero). Notice that the chloride has advanced to the same depth for equal

cumulative infiltration at the soil surface. Eventually, the rate of advance of the depth of maximum solute concentration should approach, regardless of the initial soil water content, the constant application rate (flux) divided by the soil water content at the soil surface (Warrick et al., (1971).

Figures 10a, 10b, and 10c show the case for water and solute transport during infiltration under constant water flux into air-dry Lakeland fine sand. For this case, the chloride peak did not move precisely with the wetting front, but lagged behind it considerably (Figure 10b). Evans and Levin (1968), in a similar experiment, reported that chloride and sulphate peaks lagged considerably behind the wetting front for ponded water infiltration into an air-dry sand, loam soil, and clay loam soil. They stated that "an explanation of this may be advanced by considering what happens when fresh water is first ponded on the column after wetting the first few centimeters with the salty slug of water. Upon ponding, the wetting front will immediately advance; supply of water to the wetting front will tend to occur preferentially through the higher velocity pathways or pore combinations. Thus the salty water contained in these pathways will be removed and taken up (probably preferentially in the smaller pores) at the wetting front, and fresher water from the ponded supply will replace the salty water for further advance of the wetting front, this fresher water will be transported to the wetting front and taken up. The continuous operation of this process, acting over all pore sequences according to the velocity distribution, will cause the salt concentration peak to lag behind the wetting front." Accepting the explaination for the phenomenon as presented by Evans and Levin (1968), one should expect separation of the peak of the chloride

concentration and the wetting front to increase in magnitude with time and distance of travel of the wetting front. Results presented by Evans and Levin (1968) and those presented here are in agreement even though the boundary conditions were different.

Figures 10c, 11c, and 12c show the effect of the initial soil-water content upon the movement of 2,4-D for a surface water flux of 2 cm/hr. The 2,4-D distributions were observed to move nearly independently of the initial soil-water content, as did the chloride distributions; however, the 2,4- distributions lagged behind the chloride due to the adsorption on Lakeland soil. Also, the tailing of 2,4-D distributions in soil solution can be explained on the basis of the non-singularity of its adsorption-desorption on the surface of soil particles. Because of the irreversible nature of adsorption-desorption tailing occurred because desorption appeared to proceed more slowly than did adsorption.

SUMMARY AND CONCLUSIONS

A laboratory study was conducted to evaluate the influence of irrigation intensity and initial soil water content upon the movement of two surface applied solutes, Cl and 2,4-D herbicide, during infiltration through a soil column. The soil was the top 15-cm of a profile classified as Lakeland fine sand. During infiltration soil solution samples were collected, soil-water contents were measured by gamma ray attenuation and soil-water suctions were measured with a tensiometer-pressure transducer system at various soil depths. Equilibrium adsorption-desorption between 2,4-D herbicide and Lakeland sand was measured and characterized by the Freundlich equation. Dispersion coefficients of Cl and 2,4-D were measured within a range of pore water velocities using the miscible displacement technique. Thin layer and gas chromatographic analyses were used to detect possible microbial and/or chemical breakdown of 2,4-D herbicide in the soil columns during displacement.

Water, chloride, and 2,4-D herbicide distributions were measured for three water application rates (2.0, 4.0, and 8.0 cm/hr) and three initial soil-water contents (0.012, 0.109, and 0.202 cm^3/cm^3). Chloride and 2,4-D herbicide movement through Lakeland soil was concluded to be independent of the soil-water content prior to infiltration for identical soil surface flux.

The effect of the soil-water application rate on the movement of chloride and 2,4-D during infiltration was evaluated by using three flux rates. The depth to which chloride and 2,4-D were moved for a given quantity of infiltrated water was found to be dependent on the rate at

which surface water was applied. Decreasing the soil-surface water content by reducing the water application rate resulted in a deeper displacement of chloride and 2,4-D for the same accumulative infiltration. This observation should be considered during irrigation management of Lakeland sand.

Due to the adsorption of 2,4-D on Lakeland soil its concentration distributions lagged behind the chloride during all column experiments, even though the chloride and 2,4-D were applied together on the soil surface.

A numerical mathematical solution developed by Salim et al. (1974) which utilized the assumption that the solute dispersion coefficient decreases with decreasing liquid pore velocity successfully predicted the position of water and chloride distributions in Lakeland soil utilizing the experimentally evaluated hydraulic conductivity, soil water diffusivity, and chloride dispersion coefficient parameters. However, when this numerical solution was used to predict the position of 2,4-D in soil profile, the calculated results did not adequately describe the measured herbicide distributions.

APPENDIX

Program to calculate θ and ρ using HP model 9100B calculator

Program Step	Code	Program Step	Code
0 0	20	3 9	01
0 1	41	3 a	00
0 2	60	3 b	00
0 3	44	3 c	40
0 4	77	3 d	40
0 5	34	4 0	00
0 6	07	4 1	02
0 7	00	4 2	11
0 8	40	4 4	01
0 9	13	4 5	00
0 a	44	4 6	06
0 b	34	4 7	00
0 c	00	4 8	05
0 d	00	4 9	02
1 0	40	4 a	01
1 1	40	4 b	20
1 2	40	4 c	40
1 3	40	4 d	40
1 4	40	5 0	02
1 5	40	5 1	05
1 6	40	5 2	05
1 7	40	5 3	07
1 8	40	5 4	01
1 9	02	5 5	06
1 a	06	5 6	03
1 b	20	5 7	03
1 c	40	5 8	10
1 d	40	5 9	07
2 0	40	5 a	02
2 1	40	5 b	20
2 2	40	5 c	40
2 3	40	5 d	40
2 4	40	6 0	01
2 5	06	6 1	01
2 6	01	6 2	03
2 7	02	6 3	03
2 8	05	6 4	03
2 9	05	6 5	07
2 a	02	6 6	05
2 b	20	6 7	11
2 c	40	6 8	11
2 d	40	6 9	01
3 0	40	6 a	01
3 1	40	6 b	20
3 2	40	6 c	40
3 3	40	6 d	40
3 4	05	7 0	10
3 5	04	7 1	03
3 6	01	7 2	06
3 7	01	7 3	07
3 8	11	7 4	04

Program Step	Code
7 5	06
7 6	06
7 7	11
7 8	03
7 9	10
7 a	02
7 b	20
7 c	40
7 d	40
8 0	40
8 1	40
8 2	40
8 3	40
8 4	40
8 5	40
8 6	07
8 7	07
8 8	11
8 9	11
8 a	01
8 b	20
8 c	40
8 d	40
9 0	40
9 1	40
9 2	40
9 3	40
9 4	40
9 5	40
9 6	40
9 7	02
9 8	05
9 9	07
9 a	00
9 b	00
9 c	40
9 d	40
a 1	00
a 2	00
a 3	00
a 4	00
a 5	00
a 6	00
a 7	00
a 8	00
a 9	00
a a	00
a b	00
a c	00
a d	00
b 0	00
b 1	00

Program Step	Code
b 2	00
b 3	00
b 4	00
b 5	00
b 6	00
b 7	00
b 8	00
b 9	00
b a	00
b b	00
b c	00
b d	00
c 0	02
c 1	02
c 2	00
c 3	00
c 4	04
c 5	11
c 6	05
c 7	02
c 8	06
c 9	02
c a	23
c b	00
c c	05
c d	00
d 0	11
d 1	00
d 2	00
d 3	10
d 4	01
d 5	01
d 6	10
d 7	00
d 8	07
d 9	01
d a	24
d b	00
d c	05
d d	07
-0 0	23
-0 1	14
-0 2	20
-0 3	01
-0 4	27
-0 5	41
-0 6	60
-0 7	44
-0 8	77
-0 9	07
-0 a	00
-0 b	40

Program Step	Code
-0 c	16
-0 d	23
-1 0	17
-1 1	67
-1 2	05
-1 3	27
-1 4	67
-1 5	06
-1 6	36
-1 7	67
-1 8	04
-1 9	27
-1 a	67
-1 b	07
-1 c	36
-1 d	25
-2 0	34
-2 1	67
-2 2	11
-2 3	36
-2 4	40
-2 5	34
-2 6	15
-2 7	17
-2 8	27
-2 9	14
-2 a	35
-2 b	67
-2 c	04
-2 d	40
-3 0	65
-3 1	36
-3 2	16
-3 3	27
-3 4	13
-3 5	35
-3 6	67
-3 7	05
-3 8	30
-3 9	65
-3 a	36
-3 b	25
-3 c	34
-3 d	67
-4 0	34
-4 1	15
-4 2	35
-4 3	67
-4 4	10
-4 5	35
-4 6	40
-4 7	34

Program Step	Code
-4 8	12
-4 9	16
-4 a	27
-4 b	13
-4 c	35
-4 d	67
-5 0	07
-5 1	30
-5 2	65
-5 3	36
-5 4	17
-5 5	27
-5 6	14
-5 7	35
-5 8	67
-5 9	06
-5 a	30
-5 b	65
-5 c	36
-5 d	25
-6 0	34
-6 1	67
-6 2	34
-6 3	15
-6 4	35
-6 5	67
-6 6	34
-6 7	12
-6 8	30
-6 9	45
-6 a	45
-6 b	44
-6 c	00
-6 d	02
-7 0	22
-7 1	04
-7 2	36
-7 3	67
-7 4	01
-7 5	36
-7 6	22
-7 7	01
-7 8	22
-7 9	76
-7 a	72
-7 b	70
-7 c	73
-7 d	34
-8 0	25
-8 1	30
-8 2	35
-8 3	02

Program Step	Code
-8 4	35
-8 5	24
-8 6	15
-8 7	67
-8 8	02
-8 9	36
-8 a	12
-8 b	34
-8 c	67
-8 d	01
-9 0	36
-9 1	30
-9 2	32
-9 3	76
-9 4	27
-9 5	02
-9 6	36
-9 7	15
-9 8	22
-9 9	36
-9 a	67
-9 b	03
-9 c	36
-9 d	01
-B 0	30
-B 1	34
-B 2	01
-B 3	31
-B 4	35
-B 5	31
-B 6	72
-B 7	70
-B 8	73
-B 9	34
-B a	25
-B b	36
-B c	67
-B d	01
-b 0	35
-b 1	02
-b 2	35
-b 3	15
-b 4	77
-b 5	46

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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